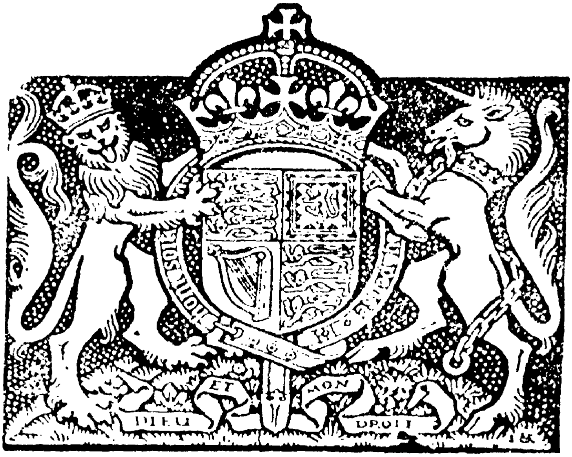

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p.	line				
175	18*	*for*	305	*read*	3 to 5
197	18	„	exhibitory	„	inhibitory
235	7	„	Hg	„	Ag
239	7	„	slugs	„	slags
243	2*	„	working again,	„	washing, again.

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JOURNAL

OF

THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*On the Estimation of Manganese in Spiegeleisen, and of Manganese and Iron in Manganiferous Iron Ores.*

By Edward Riley, F.C.S.

On the introduction and use of spiegeleisen for the manufacture of steel, the accurate determination of manganese, upon which its commercial value depends, became a question of great technical importance.

This importance has very much increased since the commencement of the manufacture of spiegeleisen in this country from the Spanish manganiferous iron ores.

Difficulties arose from the very first in fixing the percentage or number of units in spiegeleisen, in consequence of the different methods employed by chemists to estimate the manganese.

My attention having been specially directed to this question from the first introduction of spiegeleisen, about 14 years since, I purpose pointing out the causes of error, and accounting for the differences made by different chemists, and also to show the numerous sources of error that may occur, more especially in the determination of manganese, or valuation of manganiferous iron ores.

Manganese in Spiegeleisen.

There are two methods usually employed to determine the manganese in spiegeleisen; one known as the direct, the other as the indirect.

The direct method usually employed is to dissolve the pulverized spiegeleisen in dilute nitric acid (1·20 sp. gr.); when dissolved a little chlorate of potash and hydrochloric acid are added to destroy the soluble organic matter from the combined carbon. This may also be effected by evaporating the nitric acid solution to dryness, and heating, then re-dissolving in hydrochloric acid; the silica may in this case be filtered off and estimated if required. Usually, however, the percentage is so small that it is not necessary to separate it.

The solution diluted to about one quart or one litre is then neutralized with carbonate of soda or ammonia until the solution is turbid and the acid neutralized, acetate of soda or ammonia is then added, the solution boiled, the basic preacetate of iron allowed to settle, then filtered.

This precipitate is next re-dissolved in hydrochloric acid and the process repeated, the precipitate being well washed to ensure the complete separation of the manganese.

To the solution after evaporation, so as to reduce it to a bulk of about 3 pints or 1½ litres, 2 to 4 cubic centimeters of bromine are added; the solution is well agitated so as to saturate the liquid with bromine. After the bulk of it has dissolved, ·880 ammonia is added in excess, the flask in which the precipitation is made is well shaken, the manganese begins at once to separate; it is then gently heated for about one hour, up to the boiling point, boiled a few minutes, allowed to settle, and then filtered.

The precautions to be taken are to have the solution cool before adding the bromine, and to see that the solution is saturated with the bromine, otherwise the manganese is precipitated incompletely as a light brown pulverulent oxide very difficult to filter.

The filtration and washing of this precipitate (when ammoniacal salts only are used) can be effected easily in ten minutes, and the whole operation can be completed in five to six hours. Allowing the solution to stand for a night, to separate the oxide of manganese, as frequently recommended, is quite unnecessary. After filtering off the oxide of manganese, the filtrate should be evaporated down to about 1½ pints, or ¾ of a litre, and, after cooling, bromine and ammonia added, to see that the whole of the manganese is separated. If the operation is carefully carried out, it is quite the exception to find manganese in the filtrate, very rarely it occurs; if so, it must be separated and added to the first precipitate.

After drying the oxide of manganese, the filter is carefully burnt, the oxide added, and heated strongly for a quarter to half an hour, with access of air, either in a muffle, or, if over a Bunsen burner, it is advisable to finish it over a gas blowpipe.

The Indirect Method.—This method depends on the accurate determination of the iron in spiegeleisen; to this is added 5 per cent. for carbon and impurities, and the difference is assumed to be manganese.

The crushed spiegeleisen—it should be in rather fine powder for this purpose—is dissolved in dilute sulphuric, or in hydrochloric acid. After complete solution of the metal, the liquid is diluted with recently-boiled, cooled, distilled water, and the iron estimated in the ordinary way by means of a standard solution of bichromate, or permanganate of potash.

The sulphuric acid should be diluted with about three times its bulk of water. Dilute sulphuric acid is preferable to hydrochloric acid, as the sulphate of iron does not oxidise so quickly as the chloride.

As regards the first method, when it is carefully carried out, and only ammonia and acetate of ammonia used, and no fixed alkaline salts, I believe that it is the most accurate method for determining manganese in spiegeleisen.

The quantity of spiegeleisen operated on for the direct method is 15 grains, and I have a table calculated for percentages. In the indirect determinations duplicate assays are always made, taking different quantities, 15 grains and 14 grains, or in some cases 15 and 12 grains. As to the relative merits of the different standard solutions, I shall consider this and other points further on.

Many chemists seem to be unaware of the fact that one precipitation of the iron is insufficient to separate all the manganese; as the results of numerous experiments, I may state that, assuming 15 grains or 1 gramme of spiegeleisen to be operated on, the average error from only precipitating the iron once is about 1 per cent.

Take a series of determinations where identically the same crushed samples were submitted to me, and also analysed by another chemist, it will be seen that the average error was as nearly as possible 1 per cent. from this cause.

Manganese in Spiegeleisen.

No.	A.	B.	Difference.
1	12·40	11·44	·96
2	12·67	11·76	·91
3	14·18	13·26	·92
4	15·67	14·40	1·27
5	15·48	13·68	1·80
6	15·64	14·90	·74
7	15·96	14·80	1·16

Or, average error, 1·10 per cent.

I defer some other remarks on the direct determination with reference to the oxide of manganese, until the consideration of the estimation of manganese in manganiferous iron ores.

As regards the indirect determination of manganese, my experience is that the results obtained, when carefully carried out, are as a rule too low.

Take the assays of spiegeleisen exported over about nine months, the number in all about 150 determinations, the average difference of my direct assays over the indirect assays, made at the works supplying the spiegeleisen, was an excess of about 1 per cent.

For some months past the indirect method has been employed on account of the results being obtained more quickly; now there is very little difference, the results being sometimes a shade higher, at others a little lower.

The plan adopted to sample the spiegeleisen is to select four to five clean pieces from every waggon of metal; the samples, when received, varying from 20 to 150 pieces, have small fragments broken off each piece, the same weight (weighed roughly) from every piece being crushed together in a steel mortar until it all passes through a sieve with 225 holes to the square inch; for indirect assays a portion of this is more finely crushed.

By practice a man soon becomes expert, and I find no difficulty even when so many as 150 pieces are sent.

Take last year; the quantity of spiegeleisen represented by the above direct, and about as many indirect, assays was some 10,000 tons, and, I am happy to say, very few disputes arose as to yield; any that did occur were readily settled amicably, without much trouble. I mention this to show that spiegeleisen may be fairly sampled, and there is no difficulty in fixing a definite percentage in contracts for sale.

The cause of the direct assay being higher than the indirect is due to the fact that when pig iron or steel is dissolved in either dilute sulphuric acid or hydrochloric acid, a certain amount of oily hydrocarbon is formed, and soluble organic matter that acts more or less on the standard solution, thus making the iron too high, and the manganese too low.

This error is obviated when the spiegeleisen is dissolved in nitric acid, the solution evaporated to dryness, and heated to destroy the soluble organic matter. The oxides of iron and manganese should then be dissolved in hydrochloric acid, the solution largely diluted and reduced with sodium sulphite.

When this method of indirect determination is employed, the results agree very closely with the direct method, as will be seen by the series of determinations given below; whereas the difference between the ordinary indirect and direct will be seen by the table to average about ·60 to ·80 too low.

Percentages of Manganese in Spiegeleisen, estimated by different Methods.

No.	Direct estimation.	Indirect estimation by solution in sulphuric acid dil.	Difference.
1	19·43	18·70	·73
2	18·96	18·34	·62
3	19·91	19·57	·34
4	20·22	19·62	·60
5	20·89	19·98	·91
6	19·09	18·32	·77
7	20·41	20·03	·38
8	21·23	19·94	1·29
9	21·66	20·70	·96
10	21·47	21·18	·29

Mean difference in 10 assays, ·69.

The indirect determinations in the following table were made by dissolving in nitric acid, evaporating to dryness, and reducing as above described.

No.	Direct determination.	Indirect.	Difference.
1	18·56	18·41	—·15
2	17·46	17·57	+·11
3	12·29	12·04	—·25
4	16·13	15·91	—·22
5	18·50	18·83	—·33
6	18·46	18·14	—·32
7	15·69	15·62	—·07
8	14·18	14·22	+·04
9	15·67	15·59	—·08

Mean difference in 9 assays, 0·13.

All the indirect determinations by dissolving in dilute sulphuric acid were made in duplicate, the results given are the mean of the two; the difference in the two assays, as a rule, was below ·20 per cent., and never exceeded ·30 per cent.

Although this method (dissolving in dilute sulphuric acid) gives results, when carefully carried out, too low, in practice the error is in some measure compensated for by the tendency of the protoxide of iron formed in dissolving the spiegeleisen to oxidise; this is more especially the case when hydrochloric acid is used, the chloride oxidising more readily than the sulphate.

When permanganate is used, hydrochloric acid cannot be employed as a solvent.

The great merit of the indirect process is its rapidity. The time required to finish duplicate assays of a sample of crushed spiegeleisen with scientific accuracy, and using every precaution, is less than one hour, and there would be no difficulty in one operator making from 10 to 20 duplicate assays in a day, whereas the direct method requires 5 to 6 hours to carry it out efficiently.

In the indirect method, as the difference after adding 5 per cent. to the iron is considered to be manganese, it is clear that any impurities over and above the 5 per cent. will also be assumed to be manganese, and hence the actual injurious ingredients will be returned as metal. It will be seen that the consideration of the sufficiency or insufficiency of this deduction becomes of much importance.

Practically, I may say, I believe the assumption to be a fair one, on examining a series of analyses of a spiegeleisen given in the accompanying table. The percentage of manganese varying from 7 per cent. to 26 per cent. the average amount of impurities is 5·2, or rather over 5 per cent., this slightly higher percentage of impurities will, in some measure, be compensated for by the rather lower yield of manganese. The indirect method gives (page 7):—

Occasionally it will be found that the indirect method gives higher results than the direct, this is generally due to silicon; take such a spiegeleisen as No. 9 in the table, the total impurities are 6·2 per cent.

In dissolving the spiegeleisen, it can easily be observed if there is an excess of silicon, and the fact noted or a determination made of it. In this country where the ore almost universally employed is Carthagena ore, I do not think any amount of phosphorus may be anticipated, unless inferior ores have been used as a mixture.

For all practical purposes I consider the indirect method sufficiently accurate, and from the rapidity with which very approximate results can be obtained, it is a process decidedly to be recommended.

With reference to the above analyses, it will be seen that in some sulphur is given, in No. 1 as much as ·10; this is an analysis made some time ago, and I believe the sulphur to be wrong. I hold spiegeleisen and sulphur are incongruous, and the sulphur given in analyses to be derived from the reagents used, certainly it is so with spiegeleisen containing over 15 per cent. of manganese.

The question of carbon in spiegeleisen and in pig iron generally is most interesting and most important, and I certainly think it has not received the attention from chemists, and the consideration from practical men, that it merits. It is not my intention to consider the carbon question in this paper further than it is necessary as regards the composition of spiegeleisen. I may state, however, it is an element that is very badly used by chemists. To determine it accurately requires

TABLE I.—*Analyses of Spiegeleisen by Edward Riley.*

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
Iron	88·378	86·713	85·507	83·777	81·111	80·581	79·358	76·361	74·602	74·980	74·745	73·886	72·775	71·606	69·180
Manganese	6·984	8·448	9·856	11·782	13·689	14·770	15·648	18·215	19·406	19·768	20·318	20·423	22·560	22·680	26·073
Carbon	4·176	4·071	4·501	4·538	4·443	4·164	4·519	4·753	4·358	4·402	4·603	4·633	4·808	5·133	5·032
Silicon	·245	·629	·248	·041	·476	·096	·426	·375	1·546	·894	·637	·888	·476	·539	·159
Sulphur	·100	·039	·041	·010	nil	trace	·021	traces	·016	·037	·017	·022	nil	·019	nil
Phosphorus	·037	·483	·098	·084	·212	·365	·098	·059	·283	·085	·117	·064	·072	·066	·089
Copper	·424	·102	trace	·015	·080	trace	·042	traces	—	trace	—	—	·024	—	traces
	100·344	100·485	100·251	100·247	100·011	99·976	100·112	99·763	100·211	100·166	100·437	99·916	100·715	100·043	100·533
Total of elements other than iron and manganese	4·982	5·324	4·888	4·688	5·211	4·625	5·106	5·187	6·203	5·418	5·374	5·607	5·380	5·757	5·280

Mean of 14 analyses, omitting No. 9, 5·20.

TABLE II.—*Analyses of Krainische Spiegeleisen by the Krainische Company, April 1st,* 1876.

	1.	2.	3.	4.	5.	6.	7.	8.
Iron	78·01	73·50	68·71	63·27	59·00	53·39	48·17	43·85
Manganese	15·41	20·47	25·10	30·51	34·90	40·28	45·62	49·98
Carbon	5·20	4·60	4·97	4·96	4·88	4·90	4·80	3·73
Silicon	·72	·90	·80	·79	·85	·86	·91	1·98
Sulphur	·04	·03	·02	·02	·03	·02	·02	—
Phosphorus	·33	·23	·30	·28	·20	·29	·25	·22
Copper	—	—	—	—	—	—	—	—
Aluminium	·02	—	·01	·01	·01	·01	—	·02
Calcium	·10	·09	·07	·05	·08	·06	·06	·01
Arsenic	—	—	—	—	—	—	—	—
	99·83	99·82	99·98	99·89	99·95	99·81	99·83	99·79
Carbon (E.R.)	4·164 —	— —	— —	4·642 —	4·780 —	4·473 4·483	5·065 —	4·297 4·364

	I.	II.	Mean.
Carbon per cent. in ferro-manganese, 73 per cent. manganese	6·324	6·253	6·288

much time and care, and I have no hesitation in saying many determinations that are given are wrong.

The method I employ for the determination of carbon is to dissolve the pig in neutral chloride of copper; after complete solution of iron and precipitated copper, the carbon, &c., is filtered on asbestos, and burnt with oxide of copper in a current of oxygen gas.

Carbon determination by colour test for high percentages of carbon are not satisfactory.

I hold, and I purpose on a future occasion proving, that the percentage of carbon in pig iron is a measure of its quality—that is, if you have a high percentage of carbon you cannot have any sulphur, and you cannot have much silicon.

Phosphorus, I am sorry to say, it does not influence, and this, so far as my knowledge goes, still remains the *bête noire* of metallurgists.

Much difference of opinion exists as to the increase or decrease of carbon in spiegeleisen as the percentage of manganese increases. Some assert that it increases with the manganese, others that it decreases.

My experience is that the percentage of carbon increases with the percentage of manganese generally, and on this point my friend Mons. Gautier, of Terre-noire, agrees with me.

In a series of analyses sent to me, Table II, made of the spiegeleisen manufactured at the Krainische Iron Works, at Laibach, in the blast furnace, it will be seen, according to their results, that the carbon appears to decrease with the percentage of manganese.

In a series of samples received from the above-named works I have very carefully determined the carbon, and my analyses do not corroborate their views at all, although I must admit that they no not very clearly show any gradual increase beyond a certain point. Taking my analyses of spiegeleisen, Table I, the increase is fairly uniform up to 26 per cent. of manganese; my results in Table II, in the Krainische spiegel, for 30 per cent. and 35 per cent. show less carbon, but still a considerable increase on the carbon in the 15 per cent.; in the 40 per cent. and 50 per cent. the carbon is less than in the 45 per cent., so that no very positive deductions can be made from these results; in 6 and 9 the results were so anomalous that the analyses were repeated, the same results were obtained on operating on a different quantity of the spiegeleisen. To determine this point definitely a more extensive series of analyses is required.

It would also be interesting to have a series of careful analyses of ferro-manganese with a high percentage of manganese. I found in 73 per cent. ferro-manganese carbon per cent. 6·324; possibly the carbon may not always be influenced by the percentage of manganese, still the balance of testimony is, in my opinion, to the effect that carbon increases with the manganese.

There is another method that has been proposed for estimating manganese in spiegeleisen, one that would naturally suggest itself to any chemist. Mr. Parry (*Chemical News*, vol. 29, page 86) proposes one modification, Mr. Galbraith (*Chemical News*, vol. 33, page 47) another.

Some time before either of these processes were published I had tried the latter method, and found it was not satisfactory. The methods depend on the estimation of the excess of oxygen, either in the oxide Mn_2O_3 or Mn_3O_4 over and above the protoxide MnO. The question is, can you obtain absolutely and certainly either of the above-mentioned oxides. My experience is, you cannot without considerable difficulty and trouble.

The method proposed is to dissolve the spiegeleisen in dilute nitric acid, and evaporate the solution to dryness in a flask, then to heat it to redness; this operation is a troublesome one, and my experience is, that it is difficult to expel thoroughly the last traces of nitric acid.

The oxide of manganese assumed to be Mn_2O_3 (this I think rather doubtful) is then treated in the ordinary way with oxalate of soda and sulphuric acid; and the carbonic acid formed determined volumetrically or by weighing.

In the second method the oxygen is determined by adding a known weight of iron wire dissolved in acid, a certain amount of this is oxidized, and that which is left unoxidized is determined by a standard solution of bichromate of potash.

Results are given by Mr. Parry and Mr. Galbraith that certainly correspond, and I think with very great care corresponding results may be obtained; still I have found in practice the determination of the oxygen is not a desirable method.

I have made a series of careful experiments on the determination of manganese in pure sulphate of manganese, my object was partly to show how perfect and satisfactory the precipitation by bromine and ammonia is, and secondly, to see what errors may occur from insufficiently igniting the peroxide of manganese, and to prove that the definite oxide Mn_3O_4 can be obtained with care, and to show, so far as our information goes at present, it is the only reliable method we have of directly determining manganese.

Pure crystallized sulphate of manganese was finally pulverised and dried for some hours at 212° Fahrenheit (no very special precautions were taken to see that every particle of the four atoms of water were expelled, as I only wished to make comparative experiments); the results, however, all very closely coincide with the theoretical percentage, being as a rule slightly lower. If perfectly pure and dry $MnSO_4H_2O$ were used, the percentage of manganese should be 32·54 per cent.

TABLE A.

Sulphate of Manganese powdered and dried at 212° F. ($MnSO_4H_2O$).	Weights (in grains) of Proto-sesquioxide of Manganese obtained.						Difference (grains).	Manganese per cent.	Difference per cent. between Ignition over Gas and over Muffle.
Quantity (in grains) taken.	Bunsen, 15 minutes.	Bunsen, 35 minutes.	Bunsen, 65 minutes.	Bunsen, 95 minutes.	Muffle 1 hour.	Muffle 4 hours (constant).			
19 ·615	8 ·770	8 ·770	8 ·795	8 ·795	8 ·780	8 ·78 (constant)	+ ·025	32 ·25	+ ·090
19 ·335	8 ·662	8 ·662	—	—	8 ·662	8 ·662	·000	32 ·12	·000
17 ·67	8 ·085	25 minutes 8 ·085	—	—	7 ·895	—	− ·190	32 ·19	− ·770
15 ·545	7 ·120	7 ·120	—	—	7 ·020	—	− ·100	32 ·53	− ·460
13 ·52	5 minutes 6 ·025	25 minutes 6 ·045	45 minutes 6 ·065	(constant) 6 ·065	(constant) 6 ·055	(constant) 6 ·055	+ ·030	32 ·26	+ ·160
20 ·43	9 ·075	—	—	—	—	9 ·010	− ·065	31 ·77	− ·230
17 ·68	7 ·885	—	—	—	—	7 ·850	− ·035	31 ·98	− ·150
15 ·895	7 ·105	—	—	—	—	7 ·060	− ·045	32 ·00	− ·200
13 ·59	6 ·180	—	—	—	—	6 ·105	− ·025	32 ·36	− ·140
12 ·83	5 ·720	—	—	—	—	5 ·680	− ·040	31 ·96	− ·160
9 ·68	4 ·385	—	—	—	—	4 ·345	− ·040	32 ·34	− ·290

After heating the Mn_3O_4 in a muffle and weighing, the percentage of manganese was determined by estimating the extra atom of oxygen in the Mn_3O_4 over and above MnO :—

$$Mn_3O_4 = 3MnO + O.$$

On looking over the table it will be seen that taking the number of determinations, eleven in all, made on very different quantities of the salt, and made by three of my assistants, there is only one result that is at all low, 31·77 per cent.

In all these experiments the manganese was always thrown down most satisfactorily, and only in one or two cases on evaporating down the filtrate was even a trace of manganese found in it, the trace was so minute as not to be weighable. (See Table A.)

It will be seen that in some cases there was an appreciable loss in igniting the Mn_3O_4 in a muffle; I think occasionally errors are made from this cause; the oxide of manganese should be strongly heated either in a muffle or over the gas blowpipe.

On looking over the table of results by determining the oxygen, it will be seen that they are not at all satisfactory, although every care was used, some of the results obtained varied even more than those given; this is due to the fact that any very small error in the determination of the oxygen becomes a very large one on calculating out the percentage of manganese.

Some assert that oxide of manganese cannot be precipitated completely by bromine and ammonia when ammoniacal salts are present—Fresenius amongst others. This is altogether a fallacy; ammoniacal salts even in some quantity have no effect whatever in preventing the precipitation of manganese. I have proved this by destroying all the ammonia salts with fuming nitric acid, and I did not find a trace of manganese. Moreover, a most extensive experience in practically estimating manganese in many hundreds of samples—I may say thousands—fully corroborates this fact. Occasionally liquor ammonia contains tarry matter; when this has been used I find a little of the manganese is retained in solution.

Manganese Estimations.

Sulphate of manganese, $MnSO_4H_2O$ powdered and dried at 212° Fahr. quantity (in grains) taken.	Percentages of Mn.	
	By direct weight of Mn_3O_4.	By the oxidation of iron by extra atom of oxygen in Mn_3O_4.
22·286	32·51	30·21
20·430	31·77	31·51
19·615	32·25	32·76
19·335	32·12	31·57
17·680	31·98	31·34
15·895	32·00	31·37
15·628	32·29	31·53
15·230	32·73	27·96
13·590	32·36	—
12·830	31·96	31·31
9·680	32·34	—

Analyses of Spiegeleisen Cinders.

	1.	2.	3.	4.	5.
Silica	28·82	30·24	32·22	28·70	27·50
Alumina	8·35	11·70	10·95	10·25	8·60
Protoxide iron	·78	·45	·80	·38	·49
Protoxide manganese	27·29	14·74	15·53	21·23	24·13
Baryta	2·84	3·05	2·31	2·21	1·87
Lime	25·76	33·96	32·10	31·29	29·62
Magnesia	2·85	3·13	3·48	2·86	3·00
Potash	·91	·60	·46	·13	—
Sulphur	1·23 } CaS	1·09 } CaS	1·02 } CaS	1·34 } CaS	2·01 } CaS
Calcium	1·53 } 2·76	1·37 } 2·46	1·27 } 2·29	1·67 } 3·01	2·50 } 4·51
Titanic acid	traces	traces	traces	traces	traces
	100·36	100·33	100·14	100·06	99·72

Manganiferous Iron Ores.

On looking over the table of analyses of manganiferous iron ores given below, it will be seen that their composition is complex, and that they contain elements not usually found in ordinary iron ores. (See Table B.)

Hitherto the same method has been adopted for determining the manganese in these ores, as in spiegeleisen. There are, however, several of the impurities present in the ore, which are precipitated with the oxide of manganese, and very materially affect the accuracy of the results.

First, I would point out the curious fact that, as a rule, nearly all manganiferous ores contain baryta; many of them, I may say all the

TABLE B.—*Analyses of Manganiferous Iron Ores.*

	Portuguese.					Locality not known.	Carthagena.			Southern Germany.	Russian.					Italian.
	1.	2.	3.	4.	4A.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
Silica	8·25	3·70	8·15	4·25	3·88	14·90	6·22	6·99	7·97	10·60	1·50	2·40	3·50	5·90	1·52	—
Alumina	4·23	8·95	4·75	3·65	4·05	6·88	·11	·93	1·14	3·58	2·44	2·92	trace	2·08	1·25	—
Iron peroxide	22·75	23·47	45·55	23·65	23·49	12·81	45·54	36·74	39·97	35·91	·43	3·57	4·18	51·12	43·73	—
Manganese peroxide	50·70	47·15	30·88	51·73	51·73	31·77	29·62	33·81	35·80	7·02	65·21	71·46	86·20	30·51	23·57	—
Manganese protoxide	3·64	5·14	—	4·28	3·81	13·24	4·75	4·66	4·26	30·42	8·26	1·21	2·32	2·56	2·97	—
Lime carbonate	—	—	—	—	—	—	3·00	—	1·00	—	—	—	—	—	—	—
Lime	—	—	—	trace	trace	3·64	—	4·30	—	·57	trace	4·00	—	—	19·84	—
Lime sulphate	—	—	—	—	—	—	·30	—	—	—	—	—	—	—	—	—
Magnesia	trace	trace	trace	trace	trace	·70	·41	·71	·21	·42	trace	·51	traces	·40	·56	—
Baryta	—	—	—	—	—	—	—	1·09	—	—	14·87	—	—	—	—	1·09
Baryta carbonate	1·69	1·09	·34	·68	·68	1·14	—	—	·52	·44	—	—	—	—	—	—
Baryta sulphate	—	—	—	—	—	—	—	—	—	—	·34	—	—	—	—	—
Carbonic acid	—	—	—	—	—	—	—	3·42	traces	—	·59	—	—	—	—	—
Phosphoric acid	·57	·93	·55	1·45	1·45	2·30	·22	·04	·18	·33	·76	·18	·16	—	·14	—
Nickel and cobalt	—	—	—	—	—	—	—	—	—	—	·67	1·10	—	—	—	—
Sulphuric acid	—	—	—	—	—	trace	—	—	—	—	—	·04	—	—	—	—
Potash and Soda	3·20	3·20	not determined	not determined	not determined	3·94	—	—	—	—	—	—	—	—	·47	—
Combined water	4·05	5·94	6·79	5·72	5·48	4·87	6·16	8·19	8·90	9·73	4·27	7·66	2·15	6·08	3·99	—
Moisture	1·77	1·16	1·91	1·58	1·58	3·81	2·67	—	—	1·20	1·52	4·96	1·02	1·97	1·45	2·53
Zinc oxide	—	—	—	—	—	—	1·92	·54	·68	—	—	—	—	—	—	·77
	100·85	100·73	98·92	96·99	96·15	100·00	100·92	101·42	100·63	100·22	100·86	100·01	99·53	100·62	99·49	—
Iron per cent.	15·93	16·43	31·89	16·56	16·54	8·97	31·88	25·72	27·98	25·14	·30	2·49	2·92	35·78	30·61	31·10
Manganese per cent.	34·87	34·93	19·52	36·01	35·65	30·33	22·40	24·98	25·93	21·90	47·62	46·11	56·29	21·27	17·20	19·30

	I.	II.	III.	IV.
Four cargoes of ore, in which zinc was specially determined, gave zinc oxide, per cent.	·68	·68	·54	2·10

Carthagena ores, contain oxide of zinc, and I would also point out the fact that in numerous instances potash is present in a very marked quantity in manganese ores.

Take the Portuguese manganiferous ores 4 and 4A (analyses of the same sample), it was found, after analysing the ore, the results only came up to between 97 and 98 per cent. The analysis was repeated with the same result by another operator. On investigating the matter further, it was found that these ores (see 1 and 2) contained rather over 3 per cent. of potash and soda.

I may observe here the advisability in all analyses, as a rule, to determine the ingredients separately, and see that they come up to about 100, not, as is too often the case, the 100 is made up with water, organic matter, loss, &c. By my method the potash was discovered, whereas these ores were analysed by another chemist; they all came, or rather were made up, to 100, and the potash was conspicuous by its absence.

I mention this point particularly, as I propose showing that I was induced from the composition of manganiferous ores to think that probably, from the great affinity that oxide of manganese had for baryta, that baryta might be found with the oxide of manganese as ordinarily weighed in the analyses of these ores. This has been proved to be an undoubted fact. On the same reasoning, I hold that it is quite possible that oxide of manganese may in some cases take down soda or potash when these salts are used in analysis—nay, Fresenius actually mentions the fact, page 203, in the last edition by Vacher. He says: "It is impossible to convert the precipitated peroxide into protosesquioxide directly by ignition, as the residue so obtained is full of alkali, and cannot be purified by washing.

Irrespective of this, I shall show other most cogent reasons for not using any fixed alkaline salts.

It has been usual amongst chemists to use acetate of soda and neutralize by carbonate of soda in the analysis of manganiferous iron ores. Why fixed salts should be used, when volatile ammonical salts answer even better, I cannot understand, unless they took for granted the statement before referred to by Fresenius, that the ammoniacal salts prevented the precipitation of the manganese.

About ten months since Mr. John Pattinson, of Newcastle, wrote to me, enquiring whether I was aware of the fact that the manganese, as ordinarily determined, when acetate of soda was used to precipitate the iron, contained a very appreciable amount of zinc. This fact, I believe, was pointed out by Mr. Allen, of Sheffield. I wrote, in reply, stating that I did not use (nor had I used for some years) acetate of soda but acetate of ammonia, and I believed my oxide of manganese was free from oxide of zinc, but I would investigate the matter, and speak positively on the point. The ammoniacal salts would, in my opinion, prevent the precipitation of the zinc.

I very carefully examined the oxide of manganese obtained in my analyses for oxide of zinc in more than ten samples of cargoes of manganiferous ores. In all cases I found that I never obtained more than ·05 of a grain of impurities with my manganese. The method adopted was to dissolve the oxide of manganese in hydrochloric acid, add acetate of ammonia in excess, and pass sulphuretted hydrogen through the liquid. If any insoluble residue separated on dissolving in hydrochloric acid, this was filtered off and weighed.

I found the small precipitate by sulphuretted hydrogen to consist of oxide of copper, oxide of iron, occasionally oxide of lead, and a very minute trace of oxide of zinc, so small in most cases that it was impossible to recognize it as zinc.

I communicated the results of my experiments to Mr. Pattinson. He wrote, in reply, stating that he had tried the use of acetate of ammonia, and found that the oxide of manganese obtained, when this reagent was used, to be free from oxide of zinc.

I was anxious to determine the cause of the precipitation of oxide of zinc with the manganese, and made some experiments on the action of bromine on acetate of soda.

I found that nearly all samples of commercial, or so-called pure acetate of soda, were alkaline: on boiling neutral acetate of soda with bromine the solution became alkaline from the formation of carbonate of soda, and, moreover, about this time, M. Méhay (*Compt. rend.*, lxxxi, 771—773) published a paper " On the Oxidation of Acetic Acid in the Cold, in Liquids, Neutral or slightly Alkaline, containing Nitrates and Phosphates of Potassium and Sodium."

From the above it is clear that a certain amount of carbonate of soda is found in the solution in which the manganese is precipitated, and I believe this is the cause why one always obtains, when acetate and carbonate of soda are used, a very appreciable quantity of oxide of zinc, even when the percentage of zinc in the ore is not more than ·60 per cent.

Some five or six months ago I found, on examining my manganese, that the insoluble residue that in some cases remains after dissolving the oxide, hitherto considered as silica, consisted chiefly of sulphate of barium, and I further found on adding sulphuric acid to the solution, in almost every case I tried, that I obtained a precipitate of sulphate of barium, in some cases to such an extent as to have a very material effect on the yield of manganese in the sample. Taking these two causes of error, when fixed alkaline salts are used, the determination of manganese may readily be from 2 to 3 per cent. too high.

I have given a table of analyses of spiegeleisen cinder, to show that in all cases the cinder contains a little baryta. In, I believe, all previous analyses of cinder from spiegeleisen, this has been overlooked.

I am informed that on the continent, the practice is to use acetate of soda, and in cases where I have been asked to act as referee by importers of ore, this point has been urged, the reason assigned being that with ammoniacal salts, as before stated, all the manganese was not precipitated. That when acetate of soda is used, higher results are obtained, I am quite ready to admit, the cause being that oxide of zinc is precipitated frequently in some quantity with the oxide of manganese, whereas, where only ammoniacal salts are used, only traces are precipitated. Take, for example, two cargoes of ore, in which the analysis was made by acetate of soda in one case, and by acetate of ammonia in the other.

Cargo A.

	Grains of ore taken.	Mn_3O_4 obtained.	Mn_3O_4 in filtrate.	Insoluble residue in Mn_3O_4.	$BaSO_4$ by sulph. acid.	Oxide of zinc, &c.
I..	16·465	5·025	·070	·030	·20	·375
II..	17·32	4·92	—	·04	·27	·090

Cargo B.

I..	13·346	4·70	—	·210	·03	·190
II..	15·595	5·16	—	Nil.	·19	·070

Nos. I by acetate of soda, Nos. II by acetate of ammonia.

Errors in Estimation of Manganese.

Cargo A.	Due to oxide of zinc.	Due to baryta.	Total.
By acetate of soda............	1·64	·73	2·37
By acetate of ammonia	·37	·90	1·27

Errors in Estimation of Manganese.

Cargo B.	Due to oxide of zinc, &c.	Due to baryta.	Total.
By acetate of soda	1·02	1·24	2·26
By acetate of ammonia........	·32	·57	·89

I have given, in these two cargoes, the errors due to the oxide of zinc, &c., and also due to the baryta. The errors in both cases amount to from 2 to 2½ per cent. The error from the baryta is common to both processes, whereas I hold the other source of error is very small when acetate of ammonia is used.

Recently, my friend Mr. Jno. Pattinson has stated that the error may be considerable with the acetate of ammonia process. My experience does not lead me to agree with his view, and I give below the error due to the oxides of zinc, &c.

Ore taken.	Oxide of zinc &c., found.	Ore taken.	Oxide of zinc &c., found.
15·385	·085	17·02	·020
17·34	·085	16·96	·050
16·37	·015	16·625	·060
17·41	·040	16·27	·040
17·34	·040	17·05	·135
17·24	·040	17·04	·080
16·90	·050	16·50	·060
16·62	·060	16·87	·020
17·00	·045	13·82	·010
17·25	·040	14·03	·060

Average amount of oxide of zinc, &c., obtained in the above analysis from about 17 grains of ore ·051 grain = to ·21 per cent. of metallic manganese.

The above are the determinations on 20 samples of cargoes of manganiferous iron-ore. I might add many more. In only one case have I obtained more than ·10 per cent. of oxide of zinc, &c. In this cargo of ore I determined the percentage of oxide of zinc, and found it to contain 2·10 per cent. This is an unusual quantity, and to this cause is due the larger amount of precipitate obtained from the manganese.

In carrying out the analyses of these ores, one source of error is, I think, the taking too much ore to operate on, and using too concentrated solutions to precipitate the iron and manganese, and I cannot help thinking this is the cause why my friend Mr. Pattinson does in some cases obtain more oxide of zinc, &c., with his manganese than I do.

The difficulty with the baryta is one that can very easily be remedied, although, perhaps, not quite so easily as would at first be anticipated. It would naturally suggest itself to any chemist to add a few drops of sulphuric acid to the solution of the ore in hydrochloric acid; this, one would naturally think, would separate the baryta. The quantity of baryta is, however, so small as a rule, in the Carthagena ores, that it is necessary to evaporate off the excess of acid, and dilute the solution with water, allowing it to stand some hours, so as completely to separate the sulphate of barium. If this is not done, baryta will be found as sulphate with the manganese, or as baryta in adding sulphuric acid to the hydrochloric solution of it. Take a case of a cargo of ore. The percentage of baryta found was 1·34 per cent.; in 18·88 grains of this ore, dissolved in hydrochloric acid, some of the free acid evaporated off, no immediate precipitate of sulphate of barium was obtained, it was necessary to allow the solution to stand some time before the sulphate of baryta was competely separated.

In two analyses of this ore, the baryta obtained with the manganese was as below :—

	Grains.		Mn_3O_4.	Containing insoluble $BaSO_4$.	Containing soluble baryta, $BaSO_4BaO$.
Ore taken ...	15·825	gave	3·81	·085	·195 = ·128

or calculating this out 1·15 (out of 1·34 per cent.) of the baryta was found with the manganese. Thus showing that when there is only a small percentage of baryta in the ore the bulk of it is found in the manganese. Again, in the same sample :—

	Grains.		Mn_3O_4.	Containing no insoluble $BaSO_4$.	Containing soluble baryta, $BaSO_4BaO$.
Ore taken ...	14·055	gave	3·39	—	·22 = ·144

The baryta, with the manganese, amounted to 1·02 of 1·34 per cent. present in the ore. In this analysis, the solution in hydrochloric acid, after separating the silicious residue, had a few drops of sulphuric acid added to it, under the impression that the baryta would be separated and remain with the basic acetate of iron. This proved not to be the case, thus establishing the curious fact, proved also in many other instances, that the manganese carries down the baryta, when sulphuric acid fails to do so. This shows the necessity of carefully separating the baryta, and even after this, the manganese weighed should be tested to see that it is free from it. The above cargo of ore was one about which there was a dispute as to yield. To still further prove the uniformity of the precipitation of the baryta with the manganese, I give below the results of the analysis of the chemist to the works purchasing the ore.

The yield of manganese in the dry ore was :—

	Works. I.	Tucker. II.	Jarvis. III.
Metallic manganese per cent. ...	17·26	17·36	17·37

II and III are the names of my assistants. I myself made a third analysis, separating the baryta first.

After deducting baryta in Tucker and Jarvis's analyses, the percentage was :—

Metallic Manganese per cent. free from Baryta.

Tucker.	Jarvis.	Riley.	Mean of three.
16·64	16·37	16·54	16·55

The works would pay on 17·26 per cent., or pay for ·71 per cent. of baryta as manganese; or, on our results, on 17·36 per cent., or ·81 per cent. of baryta.

I should perhaps mention that the seller's assay of this cargo of iron ore was some 3 per cent. too high; this was due, I believe, to the sampling.

Take another case of a cargo of iron ore, the results obtained by the seller's chemist and my own are given:—

	Seller's chemist.	Jarvis.	Tucker.	Mean.
	23·78	23·92	23·85	—
After separating baryta—				
		23·34	22·95	23·14

The mean results of my analyses agree within $\frac{1}{10}$ per cent. with seller's analyses. On this analysis ·64 of baryta was sold as manganese; in the analyses I give ·74 per cent.

I have selected these two cases, as I have results of other chemists besides those obtained in my own laboratory. In many cargoes the error due to the baryta is over 1 per cent.: the error will, in fact, depend on the percentage of baryta present in the ore. Take an extreme case, such as the manganese in No. 10 in the table of analyses, containing 14·87 per cent. of baryta, the difference in the yield of manganese before separating the baryta and afterwards was 4·75 per cent. In another case, where the percentage of baryta was 3·36 in the ore, the quantity precipitated with the oxide of manganese was 3·15, the difference in the yield of manganese by this amount of baryta being precipitated with it, being 2·50 per cent. on the manganese.

As a rule, I find it is in the very rich manganiferous iron ores that the baryta is chiefly found. I have had very frequent cases of a difference of over 1 per cent.; this, in a cargo of ore of 1,000 tons, would make a difference of £50 in its value—a very serious item.

In calcareous manganiferous iron ores, unless some care is taken in precipitating the manganese, a certain amount of lime is carried down and weighed as manganese. In such cases it is desirable to re-dissolve the peroxide after the first precipitation, and re-precipitate it by bromine and ammonia; by this means any lime or other impurities (except baryta) will be separated.

I have tried numerous experiments on the Italian manganiferous iron ore, containing much lime, and also in the analyses of blast furnace cinder from spiegeleisen. I found that by precipitating the oxide of manganese quickly and filtering it rapidly very little lime was taken down, and that the second weighing of the manganese only gave a difference of ·30 per cent. less in the yield. If, however, great care is not taken, and if the solution is allowed to stand for the separation of the manganese, as recommended by some, then I think it quite possible for the estimation to be 1 to 2 per cent. too high. In these highly calcareous ores, and in analysing blast furnace cinder from spiegeleisen, it is certainly necessary to test the oxides of manganese carefully for lime, to see that it is practically free from it.

Having pointed out the chief sources of error in the analysis of manganiferous iron ores, I would observe that much depends on the method of carrying out the analysis. I feel certain, especially where using acetate and carbonate of soda, I could make my results vary from 1 to 2 per cent., depending upon the different manipulations of the analysis.

Again, a very frequent source of error amongst chemists is, to make duplicate analyses on the same quantity of ore, and carry out the analyses in precisely the same way. The results may agree and yet both be wrong. I hold, if an operator take the same quantity of material, in two cases, and treats them both in precisely the same way, they may agree, but it is no positive evidence that the analyses are correct. The same operator treats the same weight under precisely the same conditions, the error in the two cases will probably be the same, and there is no check on the results. In valuing manganiferous iron ores when the accurate fixing of the percentage is of such importance to both buyer and seller, I maintain that no chemist is justified in stating that his result is the one upon which the price should be fixed.

It should be corroborated by an independent observer. In cases of contract, where my analysis is agreed upon as binding between buyer and seller, I make a practice of having two analyses made by two different operators on different quantities of ore, each working quite independently in different laboratories. These results must agree within the errors of experiment, and the mean of the two is taken as the yield of the ore.

To others than chemists, the question would naturally suggest itself, that if there are all these sources of error in analysis, and it would seem that only those who had had considerable experience could carry out the analyses efficiently, that some difficulties would arise in obtaining experienced young men to make the analyses. I may relieve the minds of those who entertain this idea, although I am sorry to say that the results of chemists do differ, and they are to practical men most perplexing. I am happy to say that at some of our larger iron and steel works, and amongst those that have made the analysis of iron and steel a special study, there is a wonderful concordance in the results obtained. This on a future occasion I shall most clearly prove. The mistake is to suppose that it requires a thoroughly scientific chemist; it simply requires one who has had practice and experience in making these analyses specially, and there is no difficulty in training young men with an aptitude for analyses to make these determinations; and I have no hesitation in saying that I have in my laboratories young men who have been with me only 18 months, who will make the analyses as accurately and as quickly as I can myself, and certainly very much better than the most scientific chemists.

It is true that difficulties do occasionally arise, such as I have pointed out. They, then, require the careful consideration of those who have given a considerable amount of attention and study to analyses, which can only successfully be obtained by some years of experience.

The question of sampling the ore is of even more importance than the analysis, as without careful sampling the results of the chemist are valueless. I need hardly point this out to practical men, as their experience in this is quite as large as my own. I purpose confining my remarks to some few points in connection with it.

First: I think the samples that I receive are in some cases not judiciously taken. If the ore is not very fine, say that is contains pieces $\frac{1}{16}$ of an inch in diameter, or a trifle more than this, great care is required so as not to send an undue proportion of the larger lumps; if so, the yield will be too high, as this portion of the ore is, as a rule (not in all cases), the richest; any shaking or heaping process tends to throw the lumps on one side. The ore should be thoroughly mixed, and portions taken from different parts of the heap.

The moisture question is also an important one. It is urged by some that if the ore is pulverised finely a portion of the moisture is lost. This is undoubtedly the case if the ore is very wet, or if the pulverising takes place in warm weather, or in a warm room, some moisture may be lost. When the ore contains only 4 to 5 per cent. of water, it may be pulverised finely without any appreciable loss.

The Carthagena ores are not ores that absorb much moisture from the air, like many other ores. The average percentage of moisture in air-dried ore is about 2½ per cent.: that is to say, assuming the ore to be dried at 212° Fah., and exposed to the air, it would absorb again about 2½ per cent., whereas some highly hygrometric ores, such as Northampton, Lincolnshire, and Leicestershire ores, will absorb as much as 7½ per cent. of moisture in 48 hours when exposed to the ordinary atmosphere of a room in winter.

In giving the yield of an iron ore, it is very necessary to remember the fact that, after drying, finely powdered ores absorb by exposure to the air a considerable amount of moisture.

The plan I adopt to estimate the moisture is to open the box or bottle containing the sample of ore, and turn it out on to a balance-pan, of which I have several interchangeable in the balance. The weight is made a whole number, to make the calculations more simple, and to avoid error by having complex numbers. The quantity generally sent is from 2,000 to 4,000 grains; anything below 100 grains is put back in the box, carefully taking it from different parts of the heap. The ore is then placed in a water oven at 212° Fah., and weighed until its weight is constant, cooling it rapidly on a piece of iron. The weight, when warm, is from 5 to 7 grains less on the above-named quantities. An ordinary Avery's balance with agate knife edges, turning with about half a grain, is used, and is sufficiently accurate.

The ore, when dry, is sifted through fine muslin (adding that left in the box) the portion not passing through the sieve is pulverized in a chilled cast-iron mortar with hardened cast-steel pestle, until it all passes through the sieve. A portion of the ore, after thoroughly mixing, is then pulverized in an agate mortar and placed in the water oven for 1 to 1½ hours, it is then put into a close tube and portions weighed out for analysis.

For the determination of manganese in manganiferous iron ores, I would suggest that about 1 gram or 15 grains of the ore dried at 212° Fah. should be dissolved in hydrochloric acid, the siliceous matter separated by filtration, and the larger portion of the free hydrochloric acid driven off from the acid portion of the filtrate, reserving the washings to make the bulk of the liquid up to about one-third of a litre or half a pint, the solution should be allowed to stand four hours, to see if any baryta separates after adding previously a few drops of sulphuric acid.

If any sulphate of baryta separates it must be filtered off, if not, the analysis may be proceeded with, the solution should be diluted to about one quart or one litre, made neutral, or until the solution is slightly turbid with ammonia, and acetate of ammonia added, the solution then boiled, after boiling allowed to settle and filtered.

After filtration, and without washing, the precipitate is re-dissolved in hydrochloric acid, and again precipitated with ammonia and acetate of ammonia. The basic peracetate of iron, after settling, is filtered off and washed three or four times with boiling distilled water, adding each time a few drops of acetate of ammonia to prevent the oxide of iron passing into the filtrate and to facilitate the filtration. The filtrate must be reduced by evaporation to 1¼ litres or 3 pints, and when cold, bromine is added (2 to 4 cubic centimeters). The solution is well agitated in the flask by shaking until it is saturated with bromine, leaving only a little at the bottom undissolved, ·880 ammonia is now added in excess, shaking violently the flask, the liquid is then gradually warmed up to the boiling point for about an hour, then boiled a few minutes, the hydrated peroxide of manganese allowed to settle, then filtered off, and the precipitate dried. The filter first incinerated thoroughly, the peroxide of manganese added, heated with the lid on for a few minutes until red hot, then ignited from a quarter of an hour to twenty minutes over a Bunsen burner, or better in a muffle; if only over a Bunsen burner it should afterwards be ignited over a gas blow-pipe to see that it does not lose weight; a platinum crucible should be used, unless the ignition is made in a muffle.

The protosesquioxide of manganese (Mn_3O_4) should then be dissolved in a small quantity of hydrochloric acid. If there is any insoluble residue, which occasionally occurs, it should be filtered off; a drop or two of sulphuric acid added to see if baryta is present. If any precipitate occurs, it must be separated; to the filtrate or solution is added acetate of ammonia in excess, and sulphuretted hydrogen is passed through it to saturation.

The precipitate (a small amount is universally obtained) is filtered off and weighed. Should this weigh more than ·05 of a grain, or three millegrammes, the excess over and above this should be deducted from the oxide of manganese weighed.

I think this small amount should be allowed, as the precipitate occasionally contains traces of manganese, and the filtrate from the precipitation of the manganese by bromine and ammonia also contains a faint trace of manganese. This filtrate, in all cases, should be evaporated down to about half a litre, or nearly a pint, and tested with bromine and ammonia, to see if all the manganese is separated. As a rule, either none is obtained or a mere trace.

In making duplicate analyses, different quantities should be taken. The above-named method is the one I employ in my laboratory, and there is no difficulty in obtaining thoroughly concordant results by three different operators operating on different quantities of ore. A cargo of ore just completed gave—Tucker, 19·73; Jarvis, 19·53; Bolt, 19·69.

I have not considered some of the other processes occasionally adopted. Instead of using bromine and ammonia, chlorine is sometimes passed through the solution. After separating the iron by acetate and carbonate of soda (ammoniacal salts must not be used), the peroxide of manganese obtained (if any permanganate is formed it should be reduced with a few drops of alcohol) is re-dissolved in hydrochloric acid and precipitated with carbonate of soda. This method is much more tedious, and it has the disadvantage of using fixed alkaline salts.

The process, when sulphide of ammonia is used, is most objectionable, and I believe, as a practical method, quite out of the question; and further, I have found that when chemists have estimated the manganese by this method, very grave errors have been made.

In a cargo of ore, I found from 16·19 grains of ore taken, ·12 grain of oxide of zinc, &c., with the Mn_3O_4 weighed, thus proving the necessity of examining the oxide of manganese weighed in all cases.

I have had a lengthy correspondence with my friend, Mr. John Pattinson, of Newcastle, on the determination of manganese, more especially in manganiferous iron ores. He, like myself, has made numerous experiments, with the object of ascertaining the best method of obtaining accurate results.

Before submitting my process as the one I should recommend to be adopted by those interested in manganiferous iron ores, I have thought it desirable to have his opinion and views upon the process I have given, and cannot do better than quote his reply to me. He writes:—

"I agree with the process of testing the manganese in the main. The principal thing to insist upon is, that the Mn_3O_4 precipitate be examined for the impurities, baryta, oxide of zinc, &c.

"I do not like the principle of allowing a certain amount of impurities to be added to the precipitate to compensate for possible loss.

"The impurities I have found contain nothing like the amount of manganese you name; in fact, only inappreciable traces. Besides, if the filtrate be examined for manganese, it will be ascertained if any is left there, and anything like $\frac{1}{4}$ per cent. could not well be overlooked.

"The amount of impurities to be allowed might well be left to the judgment of the analyst.

"With this exception, you are quite at liberty to state that I agree with you in the opinion that at present this is the only correct manner of testing for manganese in these ores, and shall be obliged to you if you will do this."

From the above it will be seen that our differences are narrowed to a very small limit, practically, whether we shall or shall not allow $\frac{1}{4}$ per cent. I am quite willing to leave the settlement of this small difference to the judgment of the chemist.

Since writing the above, I have had two cases in which I found an appreciable quantity of oxide of zinc with my manganese, viz., ·13 and ·15 from about 15 grains.

The Estimation of Iron.

In the year 1862 I read a paper before the Chemical Society on the Determination of Iron (see Journal of the Chemical Society for 1862, vol. xv, page 311). I then proved the accuracy of the determination of iron by a standard solution of bichromate of potash, and showed that no gravimetrical iron estimation was satisfactory unless it had been confirmed by this or a similar method.

In England, the solution almost universally used is bichromate of potash; our neighbours on the Continent, however, as universally use permanganate of potash. Both methods may be employed, and the only question is, which is the most advantageous. After more than 25 years' experience, I unhesitatingly say the bichromate.

The chief disadvantage is, that you cannot use a hydrochloric acid solution with the permanganate, as all iron ores are soluble in hydrochloric acid (in my experience I do not think that I have met with 20 cases in which the ore would not dissolve in hydrochloric acid, if the sample were reduced to an impalpable powder), and very few in sulphuric acid; the advantage is decidedly with the bichromate.

My intention is not, however, to discuss in minute detail the relative merits of the two methods. I merely wish to make a few remarks as to the practical results of assays of cargoes of iron ore.

My experience is that the results as given are generally too high. With an average of five or six young men working in my laboratory, I find it difficult to get them to determine the exact point; when the assay is finished, it is generally slightly overdone.

Taking a given weight of pure iron wire, dissolving it, precipitating and weighing it as peroxide, then re-dissolving the peroxide in hydrochloric acid and reducing it, I find almost universally that more iron is obtained than was taken, and if calculated on the iron per cent., there is a very marked error.

In many cases referred to me, my results are generally lower, when identically the same sample is used. When, however, two chemists of equal standing, both argue that they are right, it is difficult to come to any decision.

I have recently analysed a series of about 60 samples of steel rails, and I have given, in a tabular form, the determination of the iron in these samples, first weighing the iron as peroxide after separating it from manganese, and deducting the small amount of silica usually found with peroxide of iron, and also the phosphoric acid.

It will be seen in looking over these tables that the estimation of iron as peroxide is higher than that by standard solution, and in every case in steel rails the total of all the ingredients is universally above 100 parts; hence it follows that I give the percentage of iron slightly too high, and I think that this is practical evidence of the accuracy of the method adopted; and further, I may add, it requires considerable skill in determining this iron, and, as a rule, many operators would make the standard solution rather over the peroxide of iron result, instead of *vice versâ*, as it should be.

I always use sulphite of soda as a reducing agent; I prepare it in my own laboratory, as I find the purchased salt impure and contains hyposulphite. The sulphite should always be slightly alkaline, and bisulphite should not be used.

The results obtained in using this salt are, I find, more accurate than when any other reducing agent is used for this object.

The late Mr. Ward, for many years Dr. Percy's principal assistant, after trying the various other reducing agents proposed, fully confirmed my opinion.

The table I publish, giving the results of our last year's working with standard solution, clearly shows how very near the estimations approach each other, the determination of iron in steel, and pig analysis is not only a check on the results generally, but an especial check on the phosphorus.

The same solution is used for all assays, and as the rails of which analyses are given were analysed pretty regularly throughout the year, I may say that these results are a check on all assays made during that time.

A burette with a capacity of 1,500 grains is the best. The most convenient standard I find to be from 5 to 6 grains of iron to 1,000 grains of solution, and not 10 grains, as usually employed, or on the metric system 100 cubic centimeters, equal to ·5 to ·6 of a gramme.

In carrying out the experiments in the above paper, and more especially in the accurate estimations of iron as peroxides and by standard solution, I owe much to the able assistance I have had from my senior assistant, Mr. Herdsman. In estimating iron, I have always found that when working with him on different quantities, we can always agree within ·20 per cent. I have also received most able co-operation from my other assistants, Mr. Tucker and Mr. Jarvis. Many of our analyses of cargoes of manganiferous iron ores have been repeated from three to six times, under different conditions, so as thoroughly to test the process adopted in every way.

The results given in this paper are not merely experimental results, but the practical results of every-day working, on samples from many hundred cargoes of iron ore of every description.

Determination of percentage of Iron in Steel Rails.

Iron per cent. weighed as Fe_2O_3, after deducting silica and phosphoric acid.	Iron per cent. from assay of Fe_2O_3, by standard solution of $K_2Gr_2O_7$.	Total of analysis.
99·585	99·606	100·805
99·468	99·408	100·311
99·847	99·637	100·422
99·267	99·249	100·488
99·176	99·223	100·425

Determination of percentage of Iron in Steel Rails—(continued).

Iron per cent. weighed as Fe_2O_3, after deducting silica and phosphoric acid.	Iron per cent. from assay of Fe_2O_3, by standard solution of $K_2Gr_2O_7$.	Total of analysis.
99·752	99·632	100·489
99·895	99·475	100·200
99·451	99·518	100·460
99·535	99·282	100·443
99·297	99·056	100·468
99·370	99·344	100·655
99·201	99·057	100·649
99·164	98·799	100·490
99·589	99·667	100·589
99·945	99·905	100·735
100·008	99·817	100·669
100·100	99·718	100·523
99·531	99·462	100·658
99·719	99·827	100·299
99·617	99·697	100·598
99·249	99·250	100·573
99·516	99·475	100·638
99·529	99·625	100·504
99·637	99·259	100·439
99·682	99·587	100·539
98·896	98·905	100·771
99·711	99·620	100·417
99·834	99·756	100·560
99·659	99·512	100·594
99·320	99·400	100·624
99·210	99·247	100·541
99·313	99·356	100·566
99·570	99·480	100·636
99·399	99·392	100·674
99·705	99·506	100·856
99·113	99·241	100·842
98·792	98·825	100·569
98·992	98·952	100·642
98·429	98·624	100·331
98·907	98·554	100·294
99·582	99·280	100·449
99·022	99·146	100·488
99·527	99·699	100·554
99·403	99·043	100·338
98·882	98·782	100·425

Determination of percentage of Iron in Steel Rails—(continued).

	Iron per cent. weighed as Fe_2O_3, after deducting silica and phosphoric acid.	Iron per cent. from assay of Fe_2O_3, by standard solution of $K_2Gr_2O_7$.	Total of analysis.
	99·080	99·219	100·645
	99·142	98·964	100·450
	99·334	99·199	100·536
	99·414	99·271	100·495
	99·270	99·058	100·332
	99·094	99·036	100·338
	98·627	98·779	100·390
	99·187	99·030	100·366
	99·030	98·981	100·458
Soft metal	100·259	100·291	100·674
Do.	100·207	100·154	100·281
Do.	99·844	99·891	100·285
	5,666·884	5,662·768	5,729·480
Mean	99·419	99·346	100·517
Mean difference..	—	·073	—

II.—*On some Points in Gas Analysis.*

By J. W. Thomas.

Having experienced considerable difficulty in determining the nature of a gaseous mixture which I obtained during the examination of the gases occluded in Bovey lignite, owing to the results being discordant, I undertook some experiments in order to determine the action of the reagents used for absorption in gas analysis, more especially the action of different gases upon pyrogallic acid in the presence of (KHO) potash and potassic carbonate ($COKO_2$).

In the instance of the gaseous mixture referred to, there was, after the removal of carbonic acid (CO_2), an absorption by pyrogallic acid equal to from 1·3 to 3·8 per cent. in different experiments on the same mixture. This discrepancy, together with an almost absolute certainty that no oxygen was present, led me to make the following experiments, the results of which tended to prove, as was afterwards confirmed, that the absorption by pyrogallic acid and KHo was not due to oxygen but nitric oxide (N_2O_2). Some gases which I have been examining recently, consisted almost entirely of CO_2, and in order to arrive at the nature of the remainder, some 20, 30, and even 50 c.c. of gas was used. This entailed the use of a rather large quantity of KHo, and being unable to find any decisive record whether pyrogallic acid did or did not liberate CO_2 from alkaline carbonates under varying conditions, I began by trying the effect of pyrogallic acid upon a concentrated solution of $COKo_2$. About 1 c.c. of $COKo_2$ sol. was passed up by the usual pipette into a laboratory tube of a gas apparatus somewhat similar to McLeod's, and about ·3 c.c. of a concentrated solution of pyrogallic acid added. After the lapse of two hours no gas was liberated, and apparently no action whatever had taken place. About 1 c.c. more pyrogallic (in future abbreviated to "pyro.") acid was introduced and left for four hours; no action was perceived, and no gas was liberated. As sodic hydrate is sometimes employed for absorbing CO_2 in gas analysis (I, however, prefer KHo, and always use it), I passed up 1 c.c. of a saturated solution into the laboratory (lab.) tube, and placed it under like conditions to the $COKo_2$ with pyro., and obtained a like result. The proportions of alkaline carbonate and pyro. were varied, but in no case was any CO_2 or any other gas liberated. In "Watts's Dictionary" (vol. iii, page 759) it is stated that pyro. liberates CO_2 from the alkaline carbonates, and also that Rosing states that it does not liberate CO_2 from any carbonates. My experiments confirm those of Rosing.

The action of O upon a solution of $COKo_2$ and pyro. was next tried, and to this end 7·3 c.c. of pure O was measured in the eudiometer and transferred to the lab. tube, into which the mixture of $COKo_2$ and pyro. was previously introduced. Absorption of the O took place, but only at a slow rate. After the expiration of an hour only a small bubble remained, and this very shortly disappeared almost entirely, leaving a far from measurable quantity. After carrying out a number of experiments in this direction, I found that when the volume of $COKo_2$ sol. was in large excess over the pyro. the absorption of O took place more rapidly, and with very good results. It was not, however, sufficiently rapid for use to replace the hydrate, even when practicable. An orange-brown precipitate is formed by the action of O on pyro. in the presence of $COKo_2$ or $CONao_2$. The per cent. of O in air was determined by absorbing with pyro. and $COKo_2$, the quantity of the acid being in excess. After one hour 20·1 per cent. of O had been absorbed, and although the absorption was continued for several hours afterwards the per cent. of O did not exceed that given, but after four hours appeared slightly less. Another experiment was tried with air, using again an excess of pyro. over the $COKo_2$. The absorption was slow, and there was evidently a quantity of gas evolved by the pyro. as the per cent. of O after 18 hours' absorption reached only 19·05; there was no free O left. Two other analyses were made with air and the same reagents, but twice as much $COKo_2$ as pyro. was used. The O was absorbed more rapidly than in the previous experiments, and the results were very concordant, viz., 20·97 and 20·98 per cent. The air was left in contact with the absorbents all night.

In order to ascertain the effect of using an excess of pyrogallic acid to absorb O in a gaseous mixture from which a large volume of CO_2 had been previously removed by KHo, some $COKo_2$ was introduced into the lab. tube, then a small quantity of KHo, and afterwards a solution of pyro. equal to rather more than the vol. of $COKo_2$ and KHo. A measured quantity of air was used for the experiment, and the absorption of O continued for one-quarter of an hour, a slow current of Hg dropping into the lab. tube during the time. The per cent. of O absorbed was 19·63. The remaining gas was retransferred to the lab. tube, and subjected to the action of the absorbents for ten minutes, and then measured, and the per cent. of O absorbed was found to be 20·5. In a second experiment with air about 4 parts of $COKo_2$, 2 parts KHo, and 2 parts pyro. were used for the absorption of O; after 15 minutes the per cent. of O absorbed was found to be 20·53; after another 10 minutes' absorption, 20·7 per cent., but did not exceed this by prolonged contact. In a third experiment with air, about 3 parts $COKo_2$, 2 parts KHo, and 2 parts pyro. were employed to absorb the O; after five minutes the per cent absorbed was 19·71; after five minutes more, 20·6 per cent.; and after another five minutes 20·72 per cent., which was not exceeded. In a fourth experiment with air 2 parts $COKo_2$, 2 of KHo, and 1 of pyro. were used, and the absorption continued for ten minutes, when 20·9 per cent. of O was found to be absorbed. The above experiments were repeated, and the results of a great number of trials showed that it is possible to obtain good results in the presence of $COKo_2$, when an excess of KHo over the pyro. used is present. To test the above results more completely, pure O was used in quantity about 10 c.c., and the results obtained confirmed those enumerated above.

Having, some years ago, observed that the absorption of O took place more rapidly, and more absolutely too, when the quantity of KHo was in excess of that of the pyrogallic acid used, I repeated the experiments under varying conditions. Calvert, Boussingault, and Cloez (*Jahresb.*, 1863, p. 389) found that although the absorption of O by KHo and pyro. was complete, there was always formed simultaneously more or less CO; when pure O was used the CO amounted to from 3 to 4 per cent. of its volume; and when air was used about 2·5 parts of its O was replaced by CO.

I found, as the following experiments show, that CO is generated under nearly all circumstances, but the quantity formed is dependent upon the proportions of the absorbents used and the rapidity of the absorption. When 25 c.c. of oxygen was taken for the absorption, and twice as much pyro. as KHo employed, the per cent. of CO and traces of nitrogen which appears to be held in solution in the pyrogallic acid amounted to 3·16 per cent. In the foregoing experiment the absorption proceeded slowly. When the lab. tube was agitated and a current of Hg allowed to drop through the gas, the absorption was naturally accelerated, and the per cent. of CO left was reduced to 2·73. When the quantity of KHo was equal to that of the pyro. used, and the absorption was left at rest, the residual gas measured 2·83 per cent., and in another experiment, by agitating the lab. tube, &c., as before, it was reduced to 2·06 per cent. In another experiment with O twice as much KHo as pyro. was used, and the Hg allowed to drop through without agitating the lab. tube, the residual gas (original vol. of O = 15 c.c.) was found to be 1·26 per cent. When a small quantity of O (5 e.c.) was taken, and the absorbents in the proportion of 2 parts KHo and 1 part pyro., and the lab. tube agitated, the residual gas was too small to be transferred to the eudiometer for measurement. I consequently employed an absorption tube having a long capillary neck. Using as I did, liquid absorbents which could not be removed from the contracted end of the absorption tube, the percentage volumes in the numerous experiments which I carried out are more comparative than absolute. I found, however, that it is possible to reduce the error caused by the generation of CO to less than 0·5 per cent. by using at least twice as much KHo as pyrogallic acid, the absorption tube being continually agitated during the absorption. In all instances, whether the volume of KHo be greater or less than that of the pyro., the quantity of CO is always less when the absorption is accelerated by agitating the absorption tube. Again, when large volumes of O are taken, the absorption is not so complete, and this is always the case, no matter how much of the absorbents are used. This is also the case when only just enough pyro. to absorb the O present is introduced into the lab. tube. The result of the experiments showed that the absorption of O by pyro. and KHo takes place most rapidly when there is a large excess of the latter reagent present.

The results of a further series of experiments carried out for the purpose of replacing KHo or NaHo by some other compound to assist the absorption of O by pyro. in special cases, were not worth recording. Mention may be made, however, that KCy and pyro. and KCy saturated with $CuHo_2$ and pyro. absorb O slowly, and give good results. The residual gas in two experiments measured 1·36 and 0·98 per cent. $BaHo_2$ does not materially assist in the absorption of O by pyro. or $CaHo_2$, unless very concentrated.

Having mistaken N_2O_2 for O in a gaseous mixture containing but a very small percentage of that gas (N_2O_2), some experiments were made with KHo and pyro., in order to determine the nature of the reaction which takes place when N_2O_2 is present. I had previously noticed that N_2O_2 was absorbed by those reagents. I am not aware that the fact that N_2O_2 is absorbed by an alkaline solution of pyro. is widely known, and if it be known at all it is unfortunate that it is not recorded in the books on gas analysis, as its presence in small quantity in a gaseous mixture may be the cause of unnecessary trouble and annoyance to those who have to determine gaseous mixtures of unknown composition. N_2O_2 is absorbed most rapidly when the KHo is present in excess of the pyro. used in like manner to O, but it is slowly absorbed when those reagents are used in any proportion. It is also absorbed by pyro. in the presence of $COKo_2$. In all instances, however, a portion of gas remains, and the percentage of the residual gas depends upon the time the absorption is allowed to proceed, the quantity of the absorbents employed, and the relative proportions of the absorbents. Six experiments were carried out with N_2O_2, using varying quantities of KHo and pyro. to absorb the gas. The N_2O_2 was made from pure NO_2Ko in the manner in which N as NO_2Ho is estimated by Frankland and Armstrong's process.*

No. of experiment.	Approximate proportion of re-agents used.	Time the absorption proceeded.	Percentage of gas absorbed.
1	1½KHo . . 1 pyro (dark)	35 hours	58·20
2	2KHo . . 1 pyro (fresh)	16 „	55·92
3	2KHo . . 2 pyro „	14 „	57·90
4	2KHo . . 1 pyro „	14 „	55·54
5	2KHo . . 1½ pyro „	15½ „	57·92
6	2½KHo . . 1 pyro „	40 „	60·65

The gas which remains after the absorption, which, so far as the N_2O_2 is concerned, is absolute and complete, consists entirely of nitrous oxide, so that the reaction appears to be simply this—

$$2N_2O_2 = N_2O_3 + N_2O.$$

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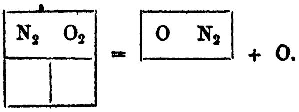
* Some time ago I communicated the result of my experiments on nitric oxide to Dr. Frankland, who suggested that the re-action between the N_2O_2 and the alkaline (caustic) solution of pyrogallic acid was simply the reduction of N_2O_2 to ON_2, by the abstraction of O, and the consequent loss of one-half its volume, thus:—



I found by experiments that no NO_2Ko or NOKo was formed. Dr. Frankland's view of the reaction is therefore correct.

During the determination of the nature of the residual gas, I observed that when N_2O is present in a gaseous mixture containing H with a large excess of O, much of the N_2O yields O to the H when a spark starts combustion, but some of the N_2O is always converted into higher nitrogen oxides.

N_2O_2 is absorbed by pyro. in the presence of $COKo_2$, but the absorption is much slower; when KHo and pyro. was used the absorption was always complete after from 7 to 10 hours; but when $COKo_2$ is substituted for KHo, the absorption is not complete for 15 hours or more. The gaseous residue is much less when $COKo_2$ is used in place of KHo, as the following experiments will show. About 2 parts $COKo_2$ and 1 part pyro. was used in both experiments. In Experiment 1 the absorption was continued for 36 hours. Small bubbles of gas were congregated around the upper portion of the Hg in the top of the lab. tube, where some of the violet compound formed was deposited, which seems to indicate that the Hg acted upon it. All the N_2O_2 was absorbed. The residual gas, which measured 14·63 per cent. of the original volume, was found to be N_2O. In Experiment 2 the absorption was continued for 15¼ hours, when 93·87 per cent. of the N_2O_2 was absorbed. The absorption was therefore incomplete, 6·13 per cent. of the N_2O_2 being present in the residual gas. The remainder of the gas, which was found to be N_2O, occupied 18 per cent. by volume of the N_2O_2 employed.

If N_2O_2 is known to be present in a gaseous mixture, then no one would look for O, but the absorption of N_2O_2 by an alkaline solution of pyro. is sufficiently rapid to prevent those reagents being used to determine which of the two, N_2O_2 or O, is present in a gaseous mixture of unknown composition. When the percentage of N_2O_2 present is large, the brown colour produced when O is added will reveal the presence of what is left after the partial absorption by KHo and pyro., but if present in small quantity, say 3 per cent., no such indication would be given. The gas absorbed by KHo and pyro. would be put down as O, and the small quantity of N_2O_2 left (owing to the absorption being incomplete) would be the means of preventing the operator from obtaining any concordant results—at least this has been my experience. Every mixture containing pyro. which I have examined absorbs N_2O_2, and I have not yet succeeded in finding an absorbent for O or N_2O_2 which will remove only one of those gases. The method which I now adopt to detect the presence of N_2O_2 is the following, but it is not applicable when Bunsen's apparatus are employed. A portion of the gaseous mixture is introduced into the lab. tube of Dr. Frankland's or McCleod's apparatus, transferred into the eudiometer, measured, and after the CO_2 is absorbed the gas is passed over into the lab. tube, which is removed, by placing a ground glass plate under it, into another Hg trough. A second lab. tube is then connected to the apparatus, some O passed up, measured in the eudiometer, and let stand therein. Lab. tube No. 2 is removed, and replaced by No. 1, containing the original gas less CO_2. There would be O in the eudiometer, and the gas in the lab. tube, both known volumes. The O is passed over into the gas, mixed by passing mercury over into the lab. tube, and the absorption continued for five minutes. The gaseous mixture is then measured in the eudiometer, and if the last measurement is less than the sum of the O + the original gas (less CO_2) then the presence of N_2O_2 may be inferred. The excess of O can now be absorbed by pyro., and the vol. of N_2O_2 noted, and the analysis proceeded with. If it is only required to know which gas is present, N_2O_2 or O, then after the removal of CO_2 the gas (after measurement) is passed over into the lab. tube, which is simply disconnected. A quantity of air is sucked into the eudiometer and measured, the lab. tube again connected, the air passed over, and any loss in volume shows the presence of N_2O_2. Some further experiments are in process of completion.

The experiments with O absorptions by KHo and pyro. in the presence of more or less $COKo_2$ may be briefly summarised thus:—

1. An excess of KHo over the pyro. employed should always be present, and the absorption accelerated by agitation.

2. When the absorption of much CO_2 by KHo has preceded that of O by pyro., it is advisable to add some more KHo, so as to have twice as much of the caustic alkali as the acid present, and if an excess of the latter has been added by accident more KHo should be passed up. The presence of $COKo_2$ does not then interfere with the absorption.

3. The alkaline solution of pyro. should be used in moderate excess, as the absorption takes place more quickly, and with the production of less CO.

4. If the reagents are used in the proportions recommended, and the absorption accelerated by agitation, the absorption will be complete in five minutes; but when much $COKo_2$ is present, it is advisable to extend the time to $7\frac{1}{2}$ or even 10 minutes, according to circumstances, while the absorption is not complete in 15 minutes if the pyro. is in excess.

I use a saturated solution of KHo and 1 part of pyro. to 5 parts of OH_2, and the word "excess" as used in this paper is not intended to convey any idea as to the combining proportion of pyrogallic acid with KHo, but simply a measurement bulk for bulk. So far as my experiments throw a light on the subject, pyrogallic acid does not appear to form any definite compound with KHo.

III.—*Experiments on the Decomposition of Nitric Oxide by Pyrogallate of Potash.*

By W. J. Russell, Ph.D., F.R.S., and W. Lapraik.

While making some experiments on gas analysis, we were led to the conclusion that nitric oxide was decomposed by pyrogallate of potash, and on further experimenting with this gas we found that this decomposition invariably takes place.

In the following experiments the nitric oxide was prepared by the action of sulphuric acid on nitrate of potash and ferrous sulphate, and the purity of the gas tested by its total absorption in a solution of ferrous sulphate. Different volumes of gas were taken, and generally from 12 to 15 hours elapsed before the decomposition of the nitric oxide was found to be absolutely complete. We naturally expected that the action of the pyrogallate would be simply to convert the nitric oxide into half its volume of nitrous oxide, but we think the following experiments clearly show that this is not the only action which takes place.

In the first three experiments the nitrous oxide was absorbed by alcohol, and in the last one it was estimated by explosion with hydrogen.

	1st expt.	2nd expt.	3rd expt.
Absorbed by pyrogallate of potash ..	59·43	58·57	58·03
„ alcohol (N_2O)	37·67	41·43	39·21
„ nitrogen..............	2·90		2·76
	100·00	100·00	100·00

Absorbed by pyrogallate of potash	58·42
After explosion with hydrogen............	38·20
„ „ nitrogen	3·38
	100·00

In all these cases more than 50 per cent. of the volume of the gas disappeared, and in all cases free nitrogen was found to be present. It will be seen, however, that the nitrous oxide and nitrogen together only amount to a little more than 40 per cent. of the volume of nitric oxide taken, still their volume is very fairly constant, viz., 40·57, 41·43, 41·97, and 41·58.

In hopes of obtaining some further insight into this reaction, we next tried the action of pyrogallate of potash, which had been fully saturated with oxygen on nitric oxide. The solution of pyrogallate was for five months exposed in a large basin to the air, and afterwards placed in a large flask full of oxygen. Some of this liquid, as in the former experiments, was allowed to act on 6·773 c.c. of nitric oxide in a eudiometer. The reaction went on from January 6th to February 12th, and then ceased.

Vol. of gas absorbed by this pyrogallate....	76·01
Vol. absorbed by alcohol, N_2O............	14·24
Nitrogen..............................	9·75
	100·00

In this case the unabsorbed gas amounted to only 23·99 per cent., and consisted of 59·36 per cent. of nitrous oxide, and 40·64 per cent. of nitrogen. We now took potash alone, and tried its action on nitric oxide. It is stated in Gmelin's Chemistry (vol. ii, page 378), on the authority of Gay-Lussac, that when nitrous oxide is kept in contact for three months with strong potash, it is resolved into one-fourth its volume of nitrous oxide, and into nitrous acid, which combines with the potash.

The following experiments agree with this statement. Both experiments were started on January 23rd, 1876. In August the action in the first experiment was still going on, and the last reading was not taken until January in this year. The second experiment where there was a smaller bulk of gas, was completed in May last.

	1st expt.	2nd expt.
Volume of gas absorbed by potash	75·28	77·02
„ unabsorbed................	24·72	22·95
	100·00	100·00

The amount of gas unabsorbed was then very nearly the same as in the last experiment.

In order to try whether this action could be much expedited by heat, we placed a tube with the gas and potash in a water-bath, and heated them continuously, until the action ceased.

This took 13 days. The experiment was made in a non-graduated tube; the result was—

Volume of gas absorbed..........	76·7
„ unabsorbed........	23·3
	100·0

To ensure the air taking no part in these long exposures, we have tried the same action in sealed tubes, and in these cases have carefully examined the residual gas. The amount of contraction produced by the potash in the tubes could be but approximately estimated, but the results are sufficiently precise to show that it is, as in the foregoing experiments, about three-quarters of the total volume. In the first experiment the diminution amounted to nearly 80 per cent., and in the second to 77·3 per cent. 5·51 c.c. of the residual gas was taken in one case, and 4·09 c c. in the other. On analysis they were found to consist of—

	1st expt.	2nd expt.
Nitrous oxide	92·02	89·68
Nitric oxide	1·45	2·66
Nitrogen	6·53	7·66
	100·00	100·00

In both cases the tubes were kept sealed for four months. Crystals of potassic nitrite separated out, adhering to the inside of the tube. Essentially then the nitric oxide, as Gay-Lussac states, is by the slow action of potash converted into nitrous acid and nitrous oxide, at the same time another decomposition takes place, possibly identical with that which gives rise to the nitrogen in the pyrogallate experiments, but apparently the action is much slower.

Two similar experiments were made in which the sealed tubes were placed in water-baths and heated for a fortnight, but kept unopened for four months; the amount of contraction in one case was about 73 per cent. In the other the composition of the residual gas was—

Nitrous oxide	82·34
Nitric oxide	2·56
Nitrogen..................	15·10
	100·00

The action of water alone on nitric oxide was also tried. The experiment was made in a sealed tube, and was in every way like the last one, only water was substituted for the solution of potash.

The tube was heated in a water-bath for a fortnight, and remained unopened for four months. The contraction the gas had undergone was 46·7 per cent., but as the decomposition was not complete nitric oxide remaining in the tube, the residual gas had the following composition:—

Nitrous oxide..............	68·10
Nitric oxide	18·38
Nitrogen..................	13·52
	100·00

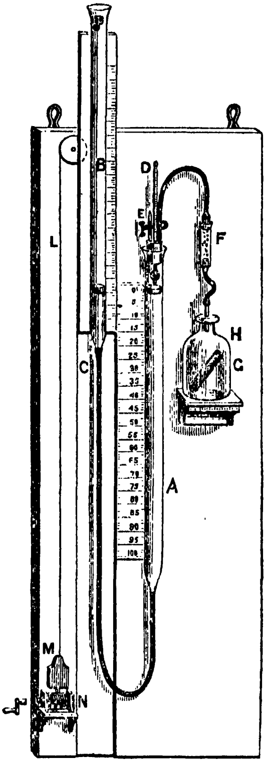
In this residue there is a great increase in the amount of nitrogen as compared to the potash experiments, but the relative quantities of nitrous oxide and nitrogen is nearly the same as in the experiment with the saturated solution of potassic pyrogallate. We find that the pyrogallic acid alone has no action on either of the oxides of nitrogen, and that alkaline pyrogallate is without action on the nitrous oxide; it seems then probable that the action of the alkaline pyrogallate is to convert the nitric oxide into half its volume of nitrous oxide, but either from the simultaneous action of the excess of potash present, or of certain compounds formed by the action of the oxygen on the pyrogallate, another and more obscure action occurs, very possibly a formation of some hyponitrite takes place. Our experiments are not, however, sufficient to establish the nature of this reaction, and for the present we wish merely to record the above results. Practically, in the analysis of the gases obtained by burning the residue from waters, it must not be assumed that a contraction of volume on the introduction of alkaline pyrogallate is a proof of the presence of oxygen.

IV.—*The Analysis of Carbonates by means of the Carbometer.*

By S. T. PRUEN and G. JONES, LL.D.

THE carbometer for the volumetric estimation of carbonic anhydride is a modification of Scheibler's well-known calcimeter, and consists of two equal and graduated glass tubes, one (A) stationary, the other (B) capable of moving in a vertical direction. These tubes are connected by a piece of vulcanized india-rubber tubing attached to the lower extremity of each. The flask (G) in which the carbonic anhydride is generated, contains a gutta-percha tube (H) for the hydrochloric acid. The two tubes are each filled with water to zero, *above* which is placed a thin layer of oil, of equal depth in both. The reason we measure the column of gas from the point where the layers of oil and water meet is because globules of oil cling to the side of the tube in descending, and thus the oil alters its relative level. The water being below the oil does not cling to the sides, and thus retains its relative level. The sliding tube (B) is attached to a thin slip of brass, which slides along a vertical groove (C) made in the board. A cord (L) fastened to this movable slip at one end, is passed over a pulley, and connected at the other end to a metal weight (M), just capable of balancing the slide when the tube attached is filled with water to zero. To this weight, which rests at the foot of the apparatus, is attached a chain band (N), wound round a roller, and equal in weight to, but twice the length of, the column of water, between the points 100 c.c. and zero in the sliding tube. A small thermometer (D) is fitted inside the upper portion of the first tube (A), passing through the india-rubber stopper, to register the temperature of the gas. A stopcock (E) is also fitted in the same place, to allow the escape of any superfluous air which may be forced in, when the stopper is fixed in the flask after it has been charged.

A chloride of calcium drying tube F intervenes between the flask and tube A.



Let us now consider the action of the apparatus during use. Taking the figures of an analysis we made in the laboratory with pure calcic carbonate.

0·2 gram of pure calcic carbonate is weighed out and introduced into the flask; the acid tube is then charged with 2 c.c. hydrochloric acid; the stopper fitted into the flask, and the stopcock E opened for a few seconds, to equalise the pressure. The temperature and pressure is then noted down, 12° C., 756 mm. bar.; and the flask gradually inclined until the whole of the acid has mixed with the sample, care being taken to grasp the flask by the neck only, in order to avoid warming it by contact with the hand.

The liberated gas, after passing through the drying tube, enters tube A, and depresses the column of liquid in it; and a corresponding amount of liquid is forced into B, which thus increases in weight, and consequently descends until it has drawn up by means of the cord and pulley a corresponding weight of chain. For instance, supposing the liquid to have been depressed 1 centimeter in A, it will have risen 1 centimeter in B. The difference between the two levels will therefore be 2 centimeters; but B will have increased in weight by a column of liquid 1 centimeter in height, and will consequently sink until it has pulled up a corresponding weight of chain, which will be 2 centimeters long; and thus the liquids in both tubes are kept nearly at the same level during the whole of the operation.

The two tubes having been accurately adjusted, the column of gas is read off. It is found to be 46·8 c.c.; to this ·16 c.c. is added, being the correction for the carbonic anhydride dissolved by the 2 c.c. of hydrochloric acid. This gives 46·96 c.c., the temperature being 12° C., and the barometer standing at 756 mm. Reducing this by the ordinary method to 0° and 756 mm. barometer, we obtain 44·76 c.c. as the true reading. Now 1 c.c. CO_2 at 0° and 760 mm. barometer weighs ·00196592 grm.; consequently when ·2 gram is taken for analysis, each cubic centimeter of gas at 0° C. and 760 mm. is equal to ·98296 per cent.; and multiplying 44·76 by ·98296 we obtain as the result of analysis, 43·99 per cent., as against the theory 44·00 per cent., showing a loss of ·01 per cent.

We have found, as the result of many analyses, that it is most convenient to use hydrochloric acid, 1 c.c. for each decigram of sample, and to calculate, according to Scheibler, ·08 c.c. as the amount of carbonic anhydride dissolved in each c.c. of hydrochloric acid.

V.—*On Certain Bismuth Compounds.* (Part V.)

By M. M. Pattison Muir, F.R.S.E., Assistant-Lecturer on Chemistry, The Owens College.

1. In the fourth part of the present series of papers I described the action of potassium ferrocyanide upon a nearly neutral solution of bismuth nitrate. This action results in the formation of bismuth ferrocyanide, $Bi_4 5FeCy_6$, a salt which, when moist and containing traces of nitric acid, readily undergoes decomposition by the action of the air.

The results of the analyses of the greenish-blue substance produced by acting on bismuth ferrocyanide with very dilute nitric acid were most readily explained on the assumption that this substance is tolerably pure bismuth ferricyanide, $Bi_3 5FeCy_6$ (*Chem. Soc. J.*, vol. i, 1877, p. 655).

2. I have now succeeded in preparing pure bismuth ferricyanide by precipitating a nearly neutral cold solution of bismuth nitrate with an excess of potassium ferricyanide, washing the precipitate with cold water by decantation, and drying over sulphuric acid *in vacuo.*

3. The salt as thus prepared presented the appearance of a tawny-yellow amorphous powder with a shade of green. It was analysed by the process described in my former paper, viz., decomposition by strong sulphuric acid, separation of bismuth by precipitation with much water, and titration of iron, after reduction, by means of permanganate. I find that instead of separating bismuth from the whole of the liquid obtained by adding water to the mass from which sulphuric acid has been for the most part expelled, it is preferable to add to this mass such a quantity of dilute sulphuric acid as suffices

to form a clear solution, to make this solution up to a determinate volume (say to ½ a litre), to withdraw an aliquot portion for the estimation of iron, to add ammonia to the remainder until the precipitate which is produced has a pale yellowish-red tint, and then to add three or four drops of acid and a considerable quantity of water. After standing some time the precipitated bismuth salts are collected, washed once or twice and dissolved in the minimum quantity of hot nitric acid. The bismuth is then determined by the ordinary gravimetric process, or by the improved volumetric method described by me in vol. I of the Society's Journal for 1877, p. 658.

As the analyses given in my former paper of the somewhat decomposed bismuth ferricyanide evidently pointed to the formula, Bi_35FeCy_6, I have not thought it necessary to make more than a single analysis of the purer preparation.

0·2793 gram gave 0·112 gram Bi_2O_3 = 0·1005 gram Bi.
0·468 „ used 8·5 c.c. permanganate = 0·0744 gram Fe.
(1 c.c. permanganate = 0·00876 gram Fe).

		Calculated for Bi_35FeCy_6.	Found.
Bismuth	=	37·29	37·18
Iron	=	16·59	15·91
Cyanogen	=	46·12	46·91 (by difference)
		100·00	100·00

4. Ferricyanide of bismuth, whether in a dry or moist condition, is unaltered in air, even after many days. If it be suspended in water and the water be boiled, hydrocyanic acid is evolved, the water acquires an acid reaction, and a green, then a greenish-blue, and finally a blue salt (or salts) is produced. The presence of small quantities of acid, more especially of nitric acid, materially hastens this decomposition of the ferricyanide. When the salt is dried at 100° it undergoes partial decomposition, with evolution of hydrocyanic acid and production of greenish-yellow substances.

5. The action of chlorine and of bromine upon ferro- and ferricyanide of bismuth respectively is interesting.

In the hope of being able to prepare ferri- from ferrocyanide of bismuth by a method other than that already described, viz., boiling with dilute nitric acid, I suspended a quantity of the nearly pure ferrocyanide (still containing traces of potash) in cold water, and passed chlorine into the mixture until the blue colour of the original salt had entirely disappeared. The liquid was now of a brownish-red colour and contained a quantity of nearly white solid matter which quickly settled to the bottom of the vessel. After filtration and washing this solid matter was found to contain bismuth and chlorine, but not a trace of iron either in the form of ferro- or ferricyanide, or of oxide. The filtrate showed the reactions of hydroferricyanic acid, but was free from hydroferrocyanic acid; on evaporation over sulphuric acid it yielded crystals of potassium ferricyanide. No bismuth could be detected in the filtrate.

6. I performed a similar experiment, keeping the water in which the ferrocyanide was suspended at the boiling point; the result was altogether different from that detailed in par. 5. The colour of the light yellow ferrocyanide slowly changed to pale blue, then to green-blue, and finally to deep blue. The supernatant liquid showed the reactions of hydroferro- and hydroferricyanic acids: it contained no bismuth. An examination of the coloured substances produced in this reaction showed that they probably consisted of more or less pure bismuth ferricyanide mixed with varying quantities of some form of prussian blue and also with bismuth oxychloride.

7. Another quantity of the ferrocyanide which contained traces of potash was suspended in cold water to which bromine was added, the whole being shaken up from time to time. Judging from the colour of the solid and liquid portions, there appeared to be a slow change of ferro- into ferricyanide of bismuth; after some hours, however, the main resultant of the action was a white precipitate containing bismuth and bromine, and a supernatant reddish-yellow liquid which exhibited the reactions of hydroferricyanic acid.

8. An experiment similar to that described in par. 6 was carried out, substituting bromine for chlorine; the result was analogous with that obtained when chlorine was employed.

9. The action of chlorine upon bismuth ferricyanide when suspended in cold and in boiling water respectively is analogous with the action of the same gas upon bismuth ferrocyanide; the decomposition of the ferricyanide is not, however, in either case so rapid as that of the ferrocyanide. The action of bromine upon the ferricyanide when suspended in boiling water is analogous with, but less energetic than, the action of the same element upon the ferrocyanide under the same conditions. If, however, ferricyanide of bismuth be suspended in cold water to which bromine is added, a complete decomposition of the salt slowly ensues, a reddish-white precipitate is produced which contains the whole of the iron and bismuth originally present in the ferricyanide, while the supernatant liquid shows no traces either of hydroferro- or hydroferricyanic acid.

10. I have examined the action of chlorine and bromine respectively upon ferro- and ferricyanide of bismuth in the presence of cold and of hot solutions of caustic soda.

The ferrocyanide is completely decomposed with the precipitation of the whole of the bismuth and iron which it originally contained. This decomposition is more rapid with bromine than when chlorine is employed; it is also more rapid in presence of hot than of cold caustic liquids. The first portions of the precipitate which is produced contain the whole of the bismuth, the solution at the same time giving the reactions for hydroferricyanic acid. If the supernatant liquid be decanted and be warmed with addition of more chlorine or bromine the decomposition is more rapid than if the action be allowed to proceed in contact with the precipitate which is at first produced. Bismuth ferricyanide is not so readily decomposed as the ferrocyanide by either chlorine or bromine in presence of caustic soda, whether hot or cold. Indeed I did not succeed in accomplishing the complete decomposition of the salt by means of chlorine even after many hours' treatment. By using a considerable excess of alkali and digesting with bromine in the cold, then pouring off the supernatant liquid, adding more bromine and gently warming, and repeating this process several times, I succeeded in effecting the complete decomposition of bismuth ferricyanide.

11. These reactions of the two double cyanides with chlorine and bromine may obviously be applied for the analysis of these salts. Bismuth ferrocyanide may be readily analysed by adding a considerable excess of caustic soda, followed by addition of bromine and heating, until the supernatant liquid when poured off from the precipitate and boiled becomes colourless; the precipitate is then collected, washed, and dissolved in sulphuric acid. The solution is divided into two portions; in one iron is determined by means of permanganate, after reduction by zinc; in the other bismuth is separated from iron, as already described, and is determined. The alkaline filtrate (containing bromine) separated from the precipitated iron and bismuth oxides may then be employed for the determination of cyanogen. This determination is most conveniently performed by the use of a standard solution of silver nitrate.

If it be desired to analyse bismuth ferricyanide by a similar process, it is advisable to digest the salt with water and bromine in the cold for some time, then to add caustic soda, to continue the digestion, to pour off the clear liquid, to add more bromine, and finally to gently warm this liquid until the decomposition is complete. The process is more applicable for the analysis of the ferro- than of the ferricyanide of bismuth.

12. Strong nitric acid when added to bismuth ferrocyanide, without warming, quickly causes the formation of bismuth ferricyanide; if the temperature be raised hydrocyanic acid is evolved and the greater part of the salt present passes into solution, evidently, however, only after undergoing decomposition.

13. If bismuth ferricyanide be suspended in water to which sodium amalgam is added the colour of the suspended salt gradually becomes paler, until an almost colourless substance is produced, which, from its general reactions, I have no doubt is bismuth ferrocyanide.

14. The action of chlorine and bromine upon ferro- and ferricyanide of bismuth respectively, as also the action of nitric acid upon the former and of sodium amalgam upon the latter salt, is, I think, in keeping with the general analogies existing between ferro- and ferricyanides. Most probably the first action of the halogens upon the ferrocyanide is to withdraw part of the bismuth with the production of hydroferrocyanic acid and bismuth ferricyanide. Hydroferrocyanic acid, it is well known, readily undergoes decomposition in the air, yielding some form of prussian blue. In the manufacture of ferricyanide of potassium the formation of a green salt is frequently noticed. This green salt, or a salt of analogous composition, would appear to be produced in many of the actions which I have described in the preceding paragraphs.

The decomposition of bismuth ferrocyanide by chlorine in presence of cold water appears at first sight to be more complete than the decomposition of the same salt by chlorine in presence of boiling water. I believe, however, that the apparent anomaly is explained by regarding—as indeed analysis shows that we must regard—the former decomposition as resulting in the production of bismuthyl chloride and hydroferrocyanic acid, while at the high temperature of the second reaction the hydroferrocyanic acid is quickly decomposed with the production of some form of prussian blue which colours the precipitated bismuthyl chloride. The rapid decomposition of the hydroferrocyanic acid produced, with subsequent precipitation of a form of prussian blue, will naturally tend to prevent the action of the chlorine upon the undecomposed ferrocyanide. The blue or green substance produced when chlorine is passed into boiling water in which bismuth ferrocyanide is suspended will therefore probably contain bismuth, ferricyanide, undecomposed ferrocyanide, bismuth oxychloride, and a form of prussian blue.

15. Ferrocyanide and ferricyanide of bismuth when heated in closed crucibles over a Bunsen lamp yield a black-brown mass containing iron, bismuth, carbon, and small quantities of cyanogen.

No. VI.—*On a Method for Detecting Small Quantities of Bismuth.*

By M. M. Pattison Muir, F.R.S.E., Assistant Lecturer on Chemistry, The Owens College.

1. In vol. lxxxviii of Poggendorff's *Annalen*, page 45, there is a paper entitled "Researches upon Bismuth," by R. Schneider. The paper is mainly concerned with a detailed account of the author's investigations upon an oxide of bismuth containing less oxygen than bismuthous oxide (Bi_2O_3). In describing one of the methods adopted for preparing this oxide, Schneider mentions the fact that a solution of bismuth in nitric acid is precipitated by addition of tartaric acid, but that the precipitate (tartrate of bismuth) so produced is soluble in caustic potash. He also shows that stannous chloride when mixed with excess of tartaric acid, and then with such a quantity of potash as is sufficient to neutralise the acid, yields a clear liquid which is unaltered on boiling or on dilution with water. He further shows that by mixing the prepared bismuth with the prepared tin solution, and adding an excess of potash, a very dark brown liquid is obtained. Schneider proves that this liquid owes its colour to the presence of dissolved hypobismuthous oxide (Bi_2O_2) contained in it.

2. As I have been lately, and am still engaged with a study of the properties of this hypobismuthous oxide (I hope to be able to lay the results before the Society at an early date), it occurred to me that a colorimetric process for estimating small quantities of bismuth might be based upon the reaction described by Schneider. On trial, however, I found that the reaction was not delicate enough to serve as the basis of a quantitative colorimetric method, but I think we have, in Schneider's reaction the means of detecting very small quantities of bismuth.

3. The test liquid I prepare as follows:* 4 grams of stannous chloride are dissolved along with 12 grams of crystallised tartaric acid in such a quantity of tolerably strong caustic potash solution as serves to produce a clear liquid having a distinctly alkaline reaction. This liquid must remain perfectly clear when it is warmed for some time to a temperature of 60° or 70°.

In order to prepare the solution which is supposed to contain bismuth for the addition of the test liquid, I add a considerable quantity of tartaric acid, warm, and then make alkaline by addition of potash. To this liquid I add a few c.c. of the test solution, warm the mixture to 60° or 70° for a few minutes, and place the beaker upon a piece of white paper. The production of a brownish-black colour shows the presence of bismuth.

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* Schneider's directions somewhat modified.

4. One part of bismuth in 210,000 parts of liquid may be thus detected.

5. I have examined the action of the stannous chloride solution upon solutions of metals other than bismuth, prepared by adding tartaric acid to an acid or neutral solution of each metal, followed by addition of excess of potash. The following are the results :—

Cadmium yields a white precipitate without any shade of brown or black.
Mercury yields a greyish-black precipitate.
Lead yields no precipitate, nor is the liquid darkened.
Copper yields a yellowish-red precipitate.
Arsenic yields no precipitate: the liquid is not darkened.
Antimony yields no precipitate: the liquid is not darkened.
Iron yields no precipitate: the liquid is not darkened.
Cobalt yields no precipitate: the liquid is not darkened.
Nickel yields no precipitate: the liquid is not darkened.
Chromium yields no precipitate: the liquid is not darkened.
Manganese yields a yellowish-red solution, which gradually darkens.

Mercury, copper, and manganese can therefore alone interfere with the reaction: the first-named metal, if present, must certainly be removed before applying the test: although the others yield precipitates or coloured solutions, yet this is only the case when they are present in comparatively large amount.

6. I had hoped to have perfected a volumetric method for determining bismuth by precipitation as hypobismuthous oxide by means of the prepared tin solution, employing mercuric chloride as an indicator, but as yet I have not succeeded.

I would propose to call the prepared tin solution "Schneider's Reagent."

VII.—*Contributions to the History of the Naphthalene Series.*
No. I. *Nitroso-β-naphthol.*

By JOHN STENHOUSE, LL.D., F.R.S., and CHARLES E. GROVES.

FUCHS (*Deut. Chem. Ges. Ber.*, viii, 625) has shown that, as in the case of phenol, an atom of hydrogen in α-naphthol can readily be directly replaced by the nitrosyl group, NO, giving rise to two isomeric nitroso-α-naphthols. He has also obtained a nitroso-β-naphthol (*ibid.*, 1026) by a similar process, but on repeating the experiment we found that not only was the dirty greenish coloured precipitate containing the nitrosonaphthol very difficult to purify, but that the yield of the nitroso compound was far from satisfactory. It seemed probable, however, that the use of nitrosyl sulphate which had answered so admirably as a nitriting agent for the preparation of nitroso-orcin and nitroso-resorcin might also give better results in this instance. A preliminary trial at once showed this to be the case.

Nitroso-β-naphthol.

On mixing dilute aqueous solutions of sodium β-naphtholate and of nitrosyl sulphate, a brilliant yellow precipitate of the nitroso compound was at once formed, but on standing, a portion of this soon rose to the surface and gradually became darker in colour, probably owing to secondary action between the nitroso-naphthol and unattacked naphthol; the portion which remained suspended in the liquid retaining its bright yellow colour. After several trials the following process was found to yield the best results: 1 part of pure β-naphthol was dissolved in 10 parts of boiling water by means of 1 part by measure of sodium hydrate solution of sp. gr. 1·323,* cooled, and poured into 100 parts of water. A nitriting solution was then prepared by pouring 2 parts by weight of the 15 per cent. nitrosyl sulphate solution previously described (this Journal, 1877, vol. I, p. 545) into 200 of water, with constant stirring, and the dilute aqueous solution of sodium β-naphtholate above mentioned was at once added and thoroughly and intimately mixed, which when small quantities were operated on was most conveniently done by pouring the liquid from one vessel into another. After standing 12 to 20 hours, the precipitate of crude nitroso-β-naphthol was collected on a linen filter and washed with cold water until the washings ceased to be acid. This precipitate when dried weighed rather more than the β-naphthol originally taken.

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* A solution of this strength contains 30 grams sodium oxide in each 100 c.c.

Fuchs purified his crude nitroso-β-compound by dissolving it in petroleum, and concentrating by distillation. This, however, is exceedingly inconvenient, as the slight solubility of the substance in petroleum renders it necessary to use very large quantities of the latter; moreover, the product obtained in this manner is far from pure. A modification of this method, however, obviating the distillation of large quantities of petroleum, was adopted in the first instance for the partial purification of small quantities of the nitroso-compound. The crude product, after being carefully dried at the ordinary temperature, or at a very gentle heat, was agitated with 200 times its weight of light petroleum at about 40° C., and filtered from the insoluble portion. A few drops of an alcoholic solution of ammonia was then added to the clear petroleum solution, which produced a bright green precipitate consisting of the ammonium compound of nitroso-β-naphthol. This was collected, and the petroleum, after removal of the excess of ammonia by agitation with dilute sulphuric acid, employed again to extract the crude product. The green ammonium compound, when exposed to the air to allow the petroleum to evaporate, gradually lost part of its ammonia, becoming yellow. The remainder of the ammonia was removed by moistening it with acetic acid, and washing with water, but the nitroso-naphthol thus obtained, even after crystallisation from boiling petroleum was still impure, and had to be converted into the sodium salt and precipitated in the manner subsequently described. As **Fuchs** states that he obtained two isomeric derivatives from α-naphthol, the nitroso-β-naphthol was submitted to a careful fractional crystallisation from petroleum, but no evidence could be obtained of the existence of a second isomeric nitroso compound.

The attempts made to purify the crude product by crystallisation from various solvents such as alcohol, ether, benzene, carbon bisulphide, acetic acid, &c., met with but indifferent success, as did also the precipitation of the alcoholic solution by ammonia or soda. The method ultimately adopted was based on the insolubility of the barium compound, which is thrown down as a bulky green precipitate on adding a solution of barium chloride to a solution of the nitroso compound in a dilute alkali. The moist crude product mentioned above as obtained from 1 part of β-naphthol was suspended in 35 parts of water, that is sufficient water was added to the moist crystalline paste to make it up to 35 parts by measure; 1 part of the 30 per cent. solution of sodium hydrate diluted with 35 of water was added to this, and the mixture agitated occasionally, and filtered after standing about an hour.*

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* In this and the subsequent operations distilled water was used, as the lime in ordinary water forms an insoluble compound with a portion of the nitroso naphthol, occasioning loss.

The clear olive-brown filtrate was then precipitated by a slight excess of a dilute solution of barium chloride,—about 1·5 parts of a cold saturated solution diluted with twice its volume of water,—and the green precipitate collected on a fine cambric filter. The reddish-brown filtrate when neutralised with an acid gave a dark-brown precipitate containing a crystalline substance: this has not been further examined as yet. The green barium compound, after being thoroughly washed, was suspended in about 35 parts of water and decomposed with hydrochloric acid in excess. The brownish-yellow, partially purified nitroso-compound was then thoroughly washed until free from barium chloride, again dissolved in dilute soda,—35 parts water and 0·5 parts, 3 per cent. solution of sodium hydrate,—filtered, precipitated as barium compound, washed, decomposed by acid, &c., as before, and the same process repeated a third time. In this way the nitroso-β-naphthol was obtained in minute needles of a brilliant yellow colour, containing water of crystallisation. They retain their colour when dried at the ordinary temperature, but may readily be converted into the anhydrous compound by crystallisation from hot spirit (5 parts): the solution must not, however, be boiled for any length of time, as decomposition would take place. The best method of recovering the nitroso-compound dissolved in the spirituous mother-liquors is to add one-tenth of its bulk of the solution of sodium hydrate; this throws down a green precipitate consisting of the sodium compound of the nitroso-β-naphthol. As the barium compound is bulky and very finely divided, it was found better when large quantities were to be operated on, to slightly modify the process just described. The barium compound first obtained (from 1 part of naphthol) after being decomposed with hydrochloric acid and thoroughly washed, was suspended in 15 parts of water, 0·5 parts 30 per cent. solution of sodium hydrate added, and the mixture heated in a water-bath. On filtering and adding one-tenth of its bulk of the soda solution, the sodium compound of the nitroso-naphthol, being almost insoluble even in comparatively dilute solutions of sodium hydrate, was thrown down as a green precipitate; this was collected, pressed, and decomposed by acid, the process of precipitation as sodium compound being repeated if necessary. The amount of pure nitroso-β-naphthol obtained in this manner is rather more than half the weight of the naphthol originally taken. A full account of the method of preparation and purification of this substance has been given, as success depends in a great measure on careful attention to details.

The anhydrous substance, crystallised from hot alcohol, and dried at the ordinary temperature *in vacuo*, was submitted to analysis with the following results:—

I. ·318 gram substance gave ·810 gram carbonic anhydride and ·119 gram water.

II. ·263 gram substance gave ·672 gram carbonic anhydride and ·100 gram water.

III. ·386 gram substance gave 27·2 cub. cent. of nitrogen at 13·5° C., and under a pressure of 751·6 mm. (corr. at 0° C.) equivalent to 25·239 cub. cent. dry nitrogen at 0° C., or ·031662 gram of nitrogen:

			Theory.	I.	II.	III.	Mean.
C_{10}	=	120	69·36	69·47	69·68	—	69·57
H_7	=	7	4·05	4·16	4·22	—	4·19
N	=	14	8·09	—	—	8·20	8·20
O_2	=	32	18·50	—	—	—	—
		173	100·00				

These numbers correspond to those required by the formula $C_{10}H_7NO_2$, or $C_{10}H_6(NO).OH$ that of nitroso-naphthol.

The hydrated nitroso-β-naphthol is of a brilliant yellow colour, and crystallises in minute needles. It is obtained in this state when any of its salts are decomposed by dilute acids, or when an alcoholic solution of the compound is poured into water. The yellow needles lose water at a gentle heat, and become brown. The anhydrous compound obtained by crystallisation from alcohol, ether, benzene, carbon bisulphide, or petroleum forms thin plates or short thick prisms of an orange-brown colour, melting at 109·5°. It is only slightly soluble in water, even when boiling, and separates almost entirely as the solution cools in long yellow needles. It dissolves very readily in carbon bisulphide, benzene, ether, acetic acid, and hot alcohol, and requires about 42 parts of alcohol at 13° for solution. It is comparatively slightly soluble in light petroleum, even when boiling.

Nitroso-β-naphthol dissolves in cold concentrated sulphuric acid with development of heat, forming a bright red solution from which the substance is precipitated unaltered on the addition of water. On strongly heating the acid solution the colour changes to brown, and the addition of water then no longer produces a precipitate, probably owing to the formation of a sulphonic acid. The nitroso-compound is decomposed when heated with concentrated nitric acid, yielding a tarry substance which dissolves on long continued boiling with the strong acid.

The compounds which nitroso-β-naphthol forms with ammonia and the alkalis are crystalline and of a bright green colour when in a finely divided state, although the masses of crystals deposited from a hot concentrated solution appear black by reflected light. The derivatives containing the metals of the alkaline earths are also of various shades of green.

Mononitro-β-Naphthol.

Although, as stated above, nitroso-β-naphthol when heated with concentrated nitric acid is decomposed and converted into tarry products, the action is different when it is submitted to the regulated action of the dilute acid at the ordinary temperature. The pure yellow crystalline hydrate was suspended in ten times its weight of water and mixed with an equal bulk of nitric acid of sp. gr. 1·25. It soon began to change in character, the yellow needles aggregating in flocks, whilst the odour of nitrous acid became distinctly apparent. In the course of an hour the precipitate had again become dense and non-coherent, the colour having changed to a yellowish-grey. It was at once collected, washed thoroughly with water, and treated with 50 parts of a cold very dilute solution of soda (1 part 30 per cent. sol. to 50 of water) and filtered from the insoluble residue. A slight excess of acetic acid was then added to the deep orange-coloured filtrate; and the bright yellow precipitate collected, washed, and crystallised once or twice from boiling alcohol in which it is very soluble. Dried in a vacuum and analysed, it gave the following results:—

I. ·215 gram substance gave ·499 gram carbonic anhydride and ·074 gram of water.

II. ·649 gram of substance gave 40·6 cub. cent. of nitrogen at 10·5° C., and under a barometric pressure of 770·2 mm. (corr. at 0°) equivalent to 39·134 cub. cent. dry nitrogen at 0° or ·049094 gram of nitrogen.

			Theory.	I.	II.
C_{10}	=	120	63·49	63·30	—
H_7	=	7	3·70	3·82	—
N	=	14	7·41	—	7·56
O_3	=	48	25·40	—	—
		189	100·00		

From these results it will be seen that the new substance, as might have been expected, is a mononitro-β-naphthol formed from the corresponding nitroso-compound by the displacement of the NO group by NO_2. This nitro-naphthol is precipitated from its solutions as a pale yellow crystalline powder apparently a hydrate. It crystallises from alcohol in orange-brown plates scarcely distinguishable in appearance from the nitroso-compound. It melts at 96°, and forms orange-coloured crystalline compounds with the alkalis and ammonia. It is more soluble than the nitroso-compound, but behaves very like the latter with concentrated sulphuric or nitric acids.

This nitro-β-naphthol, however, is not the only compound formed by the action of dilute nitric acid on the nitroso derivative, as a portion of the crude product is insoluble in dilute alkaline solutions; it is crystalline, and of a pale-yellow colour. Again, if the nitroso-β-naphthol be suspended in spirit instead of water, and then treated with dilute acid, and allowed to stand a considerable time, a greenish crystalline substance is formed almost identical in appearance with that above described. On examination, however, it was found to consist of two compounds: treatment with a dilute alkaline solution left an insoluble crystalline residue of an orange colour, whilst the addition of an acid to the filtrate threw down a pale-coloured flocculent precipitate, consisting of minute slender needles. With ammonia, the latter forms a sparingly soluble salt, crystallising in deep yellow rhomboidal plates. These substances have not been further examined as yet.

β-naphthaquinone.

When the ammonium compound of nitroso-β-naphthol was treated with hydrogen sulphide, it was reduced to an amido-compound. It was found more convenient, however, to pass hydrogen sulphide into the barium compound suspended in dilute ammonia, as the finely-divided precipitate was more readily and completely attacked than the crystalline ammonium salt; 2 parts of pure nitroso-β-naphthol were dissolved in a mixture of about 100 parts of water, with 2 of the soda solution, filtered and precipitated with barium chloride in slight excess. The precipitate, after being collected and washed, was suspended in 140 parts of water; 3 parts of ammonia solution (S.G. 0·880) were added, and hydrogen sulphide passed to saturation. At first, the barium compound assumed a more intense green colour, which, however, rapidly disappeared as the solution became saturated with hydrogen sulphide, the green precipitate being replaced by almost colourless scales of the amido-compound. After passing a gentle current of hydrogen sulphide for about an hour longer, the vessel containing the mixture was tightly corked and allowed to stand several hours, with occasional agitation. The precipitate was then collected, washed with a very dilute solution of hydrogen sulphide, and dissolved by suspending it in 140 parts of water, and adding dilute sulphuric acid in excess. It was also found advisable to add a little sulphurous acid solution, as otherwise the amido compound oxidised rapidly during filtration. The clear filtrate containing the strongly acid solution of amido-β-naphthol sulphate was immediately poured into a filtered solution of two parts of potassium dichromate in 20 of water, when the quinone at once separated in slender needles of a bright orange colour. It was collected without delay, thoroughly washed with distilled water, and dried at the ordinary temperature. It was found on incineration to contain traces of chromium; but as it decomposes very readily, it was not practicable to remove the chromium by crystallisation from any solvent. When the solutions are carefully filtered, and the operations rapidly performed, the quinone is quite pure, with the exception just mentioned. It melts at 96°. The substance was dried *in vacuo* and analysed with the following results, in which a correction has been made for the chromium present.

I. ·142 gram of substance gave ·396 gram of carbonic anhydride and ·050 gram of water.

II. ·139 gram of substance gave ·387 gram of carbonic anhydride and ·050 gram water.

			Theory.	I.	II.	Mean.
C_{10}	=	120	75·95	76·05	75·93	75·99
H_6	=	6	3·80	3·91	4·00	3·95
O_2	=	32	20·25	—	—	—
		158	100·00			

The analytical results correspond very closely with those required by the formula $C_{10}H_6O_2$, showing it to be an isomeride of the naphthoquinone previously discovered by one of us (Groves, this Journal, xxvi, 209). As its general characters and reactions moreover correspond with those of the quinones, we have called it *β-naphthaquinone*, distinguishing the readily volatile quinone formed by the direct oxidation of naphthalene or of amido-α-naphthol as *α-naphthaquinone.*

Like the ordinary quinones, β-naphthaquinone, when treated with hydriodic acid, yields a hydroquinone crystallising in colourless needles, which appeared to be reconverted into the quinone by the action of oxidising agents. The same compound is produced by the action of sulphurous acid; the quinone dissolves readily in aqueous sulphurous acid, forming a colourless solution, which deposits the hydroquinone when concentrated by evaporation at a gentle heat. When alcoholic solutions of the quinone and hydroquinone are mixed, water added, and the solution gently heated, dark-coloured crystals are deposited resembling those obtained from the corresponding α-compounds under similar circumstances. The β-naphthaquinone dissolves, when heated with dilute nitric acid, and the solution, on cooling, deposits a crystalline substance of a magnificent crimson colour. If, however, the quinone be boiled with nitric acid for some time, it is completely oxidised to phthalic acid, which may be obtained by evaporating the solution to dryness and recrystallising the residue from water. The phthalic acid readily yields a sublimate of phthalic anhydride, which, with resorcin, gives the characteristic fluorescin reaction.

Adopting Graebe's symbol for naphthalene, it is evident that both oxygen atoms in the β-quinone are in the same benzene nucleus, since it yields phthalic acid on oxidation; moreover, one of the oxygen atoms occupies the β-position, since it is a derivative of β-naphthol. The relation of the two oxygen atoms to one another is undetermined, although considering the readiness with which the quinone is attacked and decomposed, and the difficulty with which it is volatilised, it is more probable that the oxygen atoms have a meta-relation than an ortho one.

This substance is of special interest, as being the first instance of an isomeric quinone derived from the same hydrocarbon, although it should not be forgotten that in the benzene series we have a brominated compound $C_6HBr_3O_2$, the "tribromoresorquinone" of Liebermann and Dittler, which, unless the formula be doubled, is isomeric with tribromoquinone.

We purpose continuing our investigation of the new substances mentioned in this paper, and also of instituting a careful comparison of the two isomeric naphthaquinones.

VIII.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

Researches on the Reduction of Nitric Acid and the Oxides of Nitrogen. Part I. On the Gases Evolved by the Action of Metals on Nitric Acid.[*]

By J. J. Acworth and Henry E. Armstrong, F.R.S.

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[*] The substance of this paper was communicated to the Society on June 30th, 1876, and the experiments described in it were made previous to this date.

§ I. *Introductory.*—Although it is a generally recognised fact that the composition of the gases evolved when metals are dissolved in nitric acid depends not only on the metal employed, but also on the strength of the acid and the temperature at which the reaction takes place, no sufficient examination of the influence of these various factors on the nature of the gaseous product has ever been made: and what is even more remarkable, no quantitative determination of the amount of gas produced by the dissolution of a given weight of any metal in acid of a certain strength appears to have been attempted.

It is not easy to understand how so important a problem as that of the action of metals on nitric acid should have so long been regarded, we may almost say, with complete apathy by chemists. Doubtless the difficulty of collecting the gaseous product without loss and in a pure state, and of analysing the somewhat complex mixtures obtained—difficulties which are now entirely removed by the invention of those most important engines of research, the Sprengel-pump and the gas-analysis apparatus—has in part contributed to this; probably, however, it is chiefly attributable to the influence of the dogmatic teaching to which we have long been subject in these matters: for in scarcely any of our text-books is the least attempt made to explain the changes which result in the formation of the various oxides of nitrogen and of nitrogen itself. We find merely the statement that they are the products of the more or less complete deoxidation of the acid, and a single equation is invariably used to express that which undoubtedly involves a series of changes, and should therefore be represented by a series of equations; indeed, as a rule, explanatory equations are conspicuous by their absence from our text-books, and hence one of the most effective means of awakening a desire in the student to analyse the phenomena brought under his notice remains undeveloped.

The views which were long entertained with regard to the action of metals on nitric acid are succinctly stated in the following extract from Gmelin's Chemistry (*English translation*, vol. ii, 1849, p. 397):—"Nitric acid,* at ordinary temperatures or at the boiling point, oxidises all metals, excepting silicium, titanium, tantalum, platinum, rhodium, iridium, and (under ordinary circumstances) gold. The resulting metallic oxides (except those of tungsten, tellurium, tin, and arsenic) combine with the undecomposed portion of the acid and form salts. . . . . . . In this reaction the portion of acid which oxidises the metal is converted sometimes into hyponitric acid, sometimes into nitric oxide, nitrous oxide, or nitrogen gas, or—if the metal at the same time decomposes water, the hydrogen of which then combines with the nitrogen of the acid—into ammonia. Which of the above products is formed depends partly on the affinity of the metal for oxygen, partly on the temperature and concentration of the acid."

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* By *nitric acid* is here meant the compound represented by the formula NO_5 $(O = 8)$.

The explanation herein contained, although perfectly sufficient as long as the older theory of the nature of acids and of the formation of salts prevailed, ceased to be so when the acids came to be regarded as hydrogenised compounds ("hydrogen salts"); nevertheless, the language used in most chemical works, even at the present day, is almost invariably such as to lead the reader to attribute the reduction which nitric acid undergoes when acted upon by metals, to the metal itself, whereas it can scarcely be doubted that it is due, not to the direct action of the metal, but to the action of the hydrogen displaced from the acid by the metal. Miller's Elements of Chemistry (5th ed., 1874, vol. ii, p. 154), however, is the only text-book in which it is to our knowledge that this latter explanation is given.

§ II. *Theory of the Formation of the various Products obtained on dissolving Metals in Nitric Acid.*—From what is already known on the subject, and from our own experiments, we believe the following to be the most consistent and probable explanation which can be given of the formation of the gaseous and other products obtained by dissolving various metals in nitric acid.

We regard the action of the metal as consisting simply in the displacement of the hydrogen of the acid and the formation of the corresponding nitrate in the manner expressed by the following equation, in which R denotes the amount of any metal which is equivalent in combining or displacing power to two atoms of hydrogen:

$$1.\ R + 2HNO_3 = R(NO_3)_2 + 2H.$$

Under no circumstances, however, is the hydrogen thus displaced evolved as such; it at once acts on the free acid present (and even, in some cases, as we shall show later on, also on the metallic nitrate which has been formed), reducing it more or less completely to nitrous acid, nitrosidic acid,* hydroxylamine, or ammonia, as shown by the following equations:

$$2.\ HNO_3 + 2H = HNO_2 + OH_2.$$
$$3.\ HNO_3 + 4H = HNO + OH_2.$$
$$4.\ HNO_3 + 6H = NH_2(OH).$$
$$5.\ NHO_3 + 8H = NH_3 + OH_2.$$

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* We employ this name to designate the acid—if, indeed, it be an acid—the salts of which were first described by Divers in 1870 (*Roy. Soc. Proc.*, p. 425), in preference to that of hyponitrous acid, as it may be regarded as a compound of nitrosyl (NO) with hydrogen.

The gases which are evolved on dissolving metals in nitric acid result, we believe, from the decomposition of these reduction products and from their action upon each other.

The nitric oxide is chiefly, if not entirely, formed by the decomposition of the nitrous acid, in accordance with the equation:

$$6.\ 3HNO_2 = 2NO + HNO_3 + OH_2.$$

We say chiefly, if not entirely, as it is possible that some nitric oxide may be produced from the nitrosidic acid since, according to Divers, although silver nitroside ($AgNO$) is soluble in dilute nitric acid without immediate decomposition, it is immediately oxidised by the concentrated acid, copious red fumes making their appearance; and moderately diluted nitric acid decomposes it with evolution of nitrogen, and production of apparently both nitrous and nitric acids in the solution. It is also possible that hydroxylamine may furnish nitric oxide on oxidation with nitric acid.

The nitrous oxide is in all probability chiefly the product of two distinct changes, viz., *a*, of the spontaneous decomposition of nitrosidic acid, which, as Divers has shown, breaks up with the greatest readiness into nitrous oxide and water; thus:

$$7.\ 2HNO = N_2O + OH_2;$$

and *b*, of the action of nitrous acid on hydroxylamine, which, as V. Meyer has shown, takes place in the following manner:

$$8.\ NH_2(OH) + HNO_2 = N_2O + 2OH_2.$$

Finally, we regard the nitrogen as chiefly the product of the action of the nitrous acid on ammonia:

$$9.\ NH_3 + HNO_2 = N_2 + 2OH_2,$$

but it is *perhaps* in some cases in part, and in others entirely, the product of the action of nitric acid on nitrosidic acid.

The explanation we have advanced cannot be regarded as complete until the action of the various reduction-products upon each other under all the conditions which can occur in practice has been rigorously investigated—a task of no slight difficulty and magnitude; but before undertaking this, it appeared desirable to gain more definite information as to the behaviour of various metals, and especially as to the quantitative relation which the amount of gas produced bears to the amount of metal dissolved.

§ III. *Method of Experiment.*—In all our experiments we have employed weighed quantities of metal, and before bringing the latter into contact with the acid, the air has been exhausted as completely as possible from the apparatus; we have then allowed the action to take place, and have afterwards collected, not only the gas evolved spontaneously, but also that given off on repeatedly heating the nitric acid solution in a vacuum. The total quantity of gas obtained has always been measured, and its composition determined; in most cases the gas evolved during the dissolution of the metal and on subsequently exhausting previous to heating has been collected apart from that evolved on heating, and the two portions separately analysed; sometimes the gas has been pumped off at various intermediate stages of the operation and the several portions separately analysed. In this way much information has been obtained which is of value in the discussion of the sources of the gases evolved.

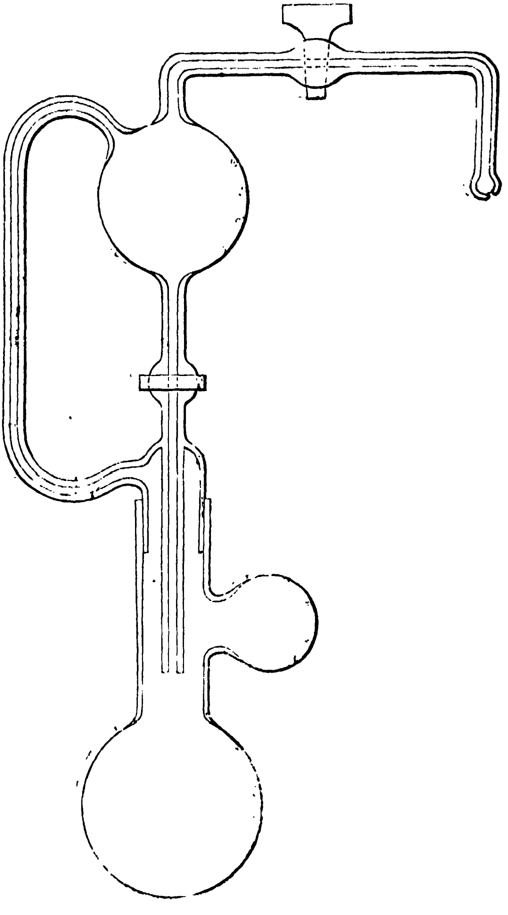
The apparatus employed in most of our experiments consisted of a glass flask formed by expanding the one end of a piece of half-inch tubing about 4 inches long into a bulb of about 25 c.c. capacity, at a short distance above which was blown on the side of the tube a small bulb or pocket for the reception of the metal, the acid being placed in the lower bulb. The flask was closed by a caoutchouc plug, through which passed a narrow glass tube, provided with a stop-cock, bent twice at right angles; by means of this tube the flask was connected with a U-tube filled with pieces of solid potassium hydroxide, the U-tube being in connection with the Sprengel-pump.

It was impossible with this apparatus to employ concentrated nitric acid on account of its action upon the caoutchouc-plug, and also on account of the metal becoming acted upon by the vapours of the acid before the exhaustion was complete. A more perfect form of apparatus was therefore devised, consisting of a flask similar to that just described, but having a ground-glass stopper through which passed the tube of a dropping funnel provided with a stop-cock. It is represented by the figure on p. 59.

Although it is not to be expected that with an arrangement of the kind described the ingress of air can be entirely prevented, we have found that if all the joints are kept covered with glycerin, the leakage is so slight in the case of the glass apparatus, that practically the result is uninfluenced thereby; but in the case of the simpler form of apparatus, there is undoubtedly an appreciable error introduced, in consequence, probably, of the diffusion of air through the caoutchouc-plug.

In making an experiment, the weighed piece of metal (as a rule foil was used) was placed in the pocket of the flask, and the acid —of which 15 c.c. were usually employed—was either poured into the lower bulb of the flask or sucked into the dropping funnel; the various parts of the apparatus having been connected together, the Sprengel-pump was set in action and the pumping continued until the exhaustion was judged sufficient, when the metal was tipped into the acid.

In most cases pumping was not re-commenced until the metal was entirely dissolved; it was then carried on as long as an appreciable amount of gas was delivered. The stop-cock in the tube connecting the flask with the U-tube containing potassium hydroxide was now closed, and the bulb of the flask surrounded with water heated to about 50°—60°; after heating it in this manner for a few minutes, it was surrounded with cold water, and when cold the stop-cock was opened and the gases which had been evolved from the solution were pumped off. This alternate heating, cooling, and removal of the gases evolved was then several times repeated, until, in fact, the quantity of gas obtained was almost inappreciable—which was usually the case after the second or third heating.



The mixture of nitric oxide, nitrous oxide and nitrogen obtained was analysed in the usual manner: the nitric oxide being determined by the addition of an excess of oxygen in presence of potassium hydroxide solution and subsequent removal of the unabsorbed oxygen by means of pyrogallol; the nitrous acid by explosion with hydrogen. It was frequently necessary to add a known volume of oxygen with the hydrogen in order to secure an explosion when the mixture consisted chiefly of nitrogen. The excess of hydrogen remaining after the explosion was usually determined in order to check the determination of nitrous oxide. The analyses were almost invariably performed in duplicate. The results of the nitric oxide determinations were almost uniformly satisfactory, but the estimation of the nitrous oxide in the extremely small amount of gas frequently remaining after the removal of the nitric oxide was not always satisfactorily effected; no difficulty, however, was experienced in the analysis of mixtures relatively rich in nitrous oxide of which a fair amount was available for combustion.

§ IV. *Mode of stating the Results.*—In order to facilitate the comparison of the results obtained with various metals and under various conditions, they are exhibited in the form of tables, in which are given the weight of metal taken; the temperature of the acid at the commencement of the experiment; the strength of the acid, of which, unless otherwise stated, 15 c.c. were always employed; the number of c.c. of gas obtained; the percentage composition of the gas; and the number of c.c. of gas per *unit-weight* of metal, *i.e.*, the quantity of metal equivalent to 2 grams of hydrogen.

§ V. *Action of Copper on Nitric Acid.*—The results of our experiments on the action of copper on nitric acid of various strengths are exhibited in Tables I and II. In discussing these results it will be necessary to consider, *a*, the composition of the gas evolved with various strengths of acid, it being remembered that, unless otherwise stated, whatever the strength of the acid, the same number of c.c. (15) of liquid was always placed in the bulb of the flask; *b*, the influence of temperature on the composition of the gas, as to which, however, we have hitherto made very few experiments; *c*, the volume of gas measured at 0° C. and under a pressure of 760 mm. of mercury obtained per unit-weight of metal; and *d*, the alteration in the composition of the gas due to the presence of varying quantities of cupric nitrate.

If the results of the experiments with acid of strength 1 : 2 (Nos. III to X inclusive) are compared, it will be seen that on the whole the composition of the gas evolved is remarkably constant, from about

I. *Action of Copper on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				c.c. of gas calc. as NO per unit-weight of metal. Theory = 14880 c.c.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
I	·35	15°	1 : 0	2·4	54·0	10·3	35·7	434				
II........	·3215	15°	1 : 1	43·48	98·17	·92	·91	8574	8417	78	78	8891
				52·22	97·97	1·33	·70					
				42·22	98·33	·87	·80					
				43·28	97·85	1·45	·70					
				42·01	98·01	1·21	·18					
				41·90	99·26	—	·74					
III	·920	13°	1 : 2	221·63	98·26	·99	·75	15272	15007	151	114	15789
				47·16	97·63	1·69	·68					
				40·41	97·82	1·47	·71					
				42·67	97·54	1·55	·91					
				40·73	97·84	1·64	·52					
				45·18	99·10	—	·90					
IV	·918	10°	1 : 2	216·15	97·99	1·21	·80	14928	14628	180	120	15508
V........	·920	11°	1 : 2	201·99	97·15	1·55	1·30	13919	13522	206	191	14707
VI	·395	11°	1 : 2	79·55	98·12	·95	·93	12768	12527	121	120	13189
VII	·1525	8°	1 : 2	20·65	96·89	·30	2·81	8584	8316	27	241	9193
VIII	·1512	11°	1 : 2	33·10	97·33	1·55	1·12	13879	13508	215	156	14267
IX	·150	50°	1 : 2	22·91	96·98	2·27	·75	9683	9390	219	74	10220

I. *Action of Copper on Nitric Acid*—continued.

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				c.c. of gas calc. as NO per unit-weight of metal. Theory = 14880 c.c.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
X........	·2285	90°	1 : 2	51·40	97·23	1·82	·95	14261	13866	259	136	15009
				46·53 16·74	93·68 95·93	4·43 1·18	1·89 2·89					
XI	·329	12°	1 : 4	63·27	94·28	3·57	2·15	12192	11494	435	263	13530
				40·43 15·03 10·70	73·30 67·40 72·91	19·90 22·30 21·80	6·80 10·30 5·29					
XII......	·325	16°	1 : 8	66·16	71·89	20·74	7·37	12845	9234	2664	947	(?) 19492
				37·34 10·45	80·07 96·53	16·07 1·57	3·86 1·90					
XIII	·2895	20°	1 : 8	47·79	83·67	12·88	3·45	10465	8756	1348	361	13552

97 to 98 per cent. being nitric oxide, the residue in all cases consisting of nitrous oxide and nitrogen. The composition of this residue appears, indeed, to be somewhat variable: but in considering the composition of the residue it is to be remembered that the apparatus cannot be completely exhausted of air before the metal is brought into contact with the acid; that probably there is a slight leakage in of air during the experiment; and that it is difficult to avoid errors in the analysis of the gas remaining after the removal of the nitric oxide, as the quantity which remains is extremely small, even if as much as 10 c.c. be analysed—and more than this was seldom employed, from 5 to 7 c.c. being the quantity usually taken for an analysis. Taking the average of the experiments, we are probably not far wrong in assuming that slightly more nitrous oxide than nitrogen is produced.

Turning now to the experiments with more concentrated and with weaker acid, it will be seen (Experiment II) that, having regard to the composition of the gas produced, the 1 : 1 acid has about the same action as the weaker 1 : 2 acid, but the result obtained with the more concentrated 1 : 0 acid (Experiment I) is very different, probably in consequence of the retention of the nitrous acid by the nitric acid. The 1 : 4 acid (Experiment XI) furnishes a gas containing only about 94 per cent. of nitric oxide, but about twice as rich in nitrous oxide as that furnished by the 1 : 2 acid. With the 1 : 8 acid (Experiments XII and XIII), the diminution in the proportion of nitric oxide and increase in the proportion of nitrous oxide and of nitrogen is very marked indeed; so that commencing with the 1 : 2 acid, it appears that nitrous oxide is produced in an increasing proportion as the strength of the acid diminishes; at the same time the rate at which the copper dissolves also diminishes, but of this we shall say more presently.

The only observations we have instituted as to the influence of temperature have been with the 1 : 2 acid. Of eight experiments with this acid, six were made by allowing the metal to dissolve in it at the atmospheric temperature; but in the other two (IX and X) the acid was heated to about 50° and 90° respectively before introducing the metal into it, after which the heating was not continued. The metal dissolved much more rapidly in the hot acid, especially in that heated to about 90°; but the gas obtained scarcely differs in composition from that generated on allowing the metal to dissolve at the ordinary temperature.

The volume of gas obtained per unit-weight of metal (63·4 grams) dissolved varies considerably, even in experiments with the same strength of acid: thus, of two experiments with 1 : 2 acid (IV and VII), the one gave 14928 c.c., and the other only 8584 c.c. This, however, is probably due to the retention of the nitrous acid in solution, for we have found that the amount of gas obtained by decomposing silver nitrite by nitric acid varies according to the strength of the acid, being greater the weaker the acid. It is always less, however, than is required, on the assumption that the nitrous acid is decomposed in accordance with the equation:

$$3HNO_2 = 2NO + HNO_3 + OH_2.$$

For example, in an experiment in which ·4493 gram silver nitrite was decomposed by 15 c.c. 1 : 2 acid, 11,975 c.c. of nitric oxide were obtained instead of 14,880 c.c. required by theory, if 1 litre of hydrogen at 0° and under the pressure of 760 mm. of mercury weigh ·089578 gram (Regnault), and 30 grams of nitric oxide are contained by a space of 22·320 litres. We may mention that the decomposition was effected in the glass apparatus shown on p. 59, and that the gas as collected contained 99·25 per cent. nitric oxide; whereas in three similar experiments made at the commencement of the investigation in which the apparatus provided with a caoutchouc stopper was employed, the gas as collected contained nearly two per cent. of nitrogen. That the decomposition of nitrous acid is especially retarded by nitric acid there can be no doubt; for if sulphuric acid be employed, the nitric oxide is given off with greater facility and in larger amount. Indeed, in three experiments which furnished closely accordant results in which silver nitrite was decomposed by a 10 per cent. solution of sulphuric acid, we actually obtained more than the required quantity of nitric oxide, viz., 15800 c.c. The amount of nitric oxide obtained depends, however, very much on the manner in which the experiment is conducted. Gas is at once given off when the acid and nitrite are brought into contact, and a further quantity is evolved as the apparatus is exhausted; but after a time the pump ceases to deliver any appreciable quantity of gas, and in order to decompose any portion of the nitrous acid remaining in solution within a reasonable time, it is necessary alternately to heat the liquid, and then to cool it and pump off the gas in the manner previously described. If weak nitric acid be employed, it is possible by repeating the heating, &c., a sufficient number of times entirely to decompose the nitrous acid in solution, but apparently no amount of heating will effect this if the acid be concentrated; it remains to be investigated whether the nitrous acid is merely held in solution by the nitric acid, or whether it is not actually combined with it—a supposition which cannot be regarded as altogether unwarranted. When copper is dissolved in nitric acid, the gas is evolved in a precisely similar manner, a portion being given off during the dissolution of the metal, a further portion on exhausting, and a very considerable proportion on heating, &c.; but the amount of nitric oxide furnished previous to the application of heat is, as a rule, less than when silver nitrite is decomposed by nitric acid, and the gas is also given off with much less facility on heating. In fact, the presence of the copper salt appears to exercise a special retarding influence on the decomposition of the nitrous acid, such as no other metal possesses of which we have examined the action on nitric acid. Thus, in the case of zinc, we have found that after the second or third heating the amount of gas evolved is inappreciable, whereas with copper a measureable quantity of gas is often obtained at the eighth or tenth heating. In Experiment VIII, for example, only about one-third of the gas collected was given off in the cold, and the heating had to be ten times repeated before gas ceased to be evolved. It is not improbable, therefore, that in certain cases in which low numbers were obtained (Experiments VII and IX), the heating, &c., was not repeated sufficiently often to entirely decompose the nitrous acid produced during the dissolution of the metal.

If the nitric oxide be, as we have supposed, derived from nitrous acid, the unit-weight of metal should furnish 14880 c.c.; thus:

$$\begin{aligned} \mathrm{Cu} + 2\mathrm{HNO_3} &= 2\mathrm{H} + \mathrm{Cu(NO_3)_2}.\\ 2\mathrm{H} + \mathrm{HNO_3} &= \mathrm{HNO_2} + \mathrm{OH_2}.\\ 3\mathrm{HNO_2} &= 2\mathrm{NO} + \mathrm{HNO_3} + \mathrm{OH_2}.\\ \therefore 3\mathrm{Cu} &= 2\mathrm{NO} \text{ or } 44{\cdot}640 \text{ litres.}\\ \text{and } \mathrm{Cu} &= \tfrac{44640}{3} \text{ or } 14880 \text{ c.c. NO.} \end{aligned}$$

It will be noticed, however, that without taking into account the relatively small quantity of nitric oxide and nitrogen obtained, slightly more than this amount of nitrous oxide appears actually to have been produced in one case (Experiment III); while in three others (Experiments IV, X, and XIV) the nitric and nitrous oxides and nitrogen together are somewhat in excess of the amount which, according to our hypothesis, can be produced. This is probably in the case of Experiments III and IV, at least in part due to the accumulation of a number of positive errors of experiment. In both the gas was collected in five portions; of each of these a portion was analysed, and if the analysis was satisfactory, the remaining portion was merely measured; while if the analysis appeared doubtful, the remaining portion was also analysed, so that the total volume is deduced from ten measurements. Moreover, as in the one experiment ·92 and in the other ·918 gram of copper was taken, any error in the measurement of the gas is multiplied nearly seventy times in calculating the volume of gas per unit weight of metal; so that a small initial error becomes magnified into a large one. This explanation, however, does not apply to Experiments X and XIV, and for the present we must hesitate to attribute the excess entirely to errors of experiment, especially since, as was above stated, we have also obtained more than the theoretical amount of nitric oxide on decomposing silver nitrite by dilute sulphuric acid; and on this account it is obviously undesirable also to attempt any further explanation until the decomposition of nitrous acid under various conditions has been carefully studied.

One of us has previously shown (*J. J. Acworth*, this Journal, 1875, p. 830), *that when nitric oxide is prepared in the ordinary manner by acting on copper with nitric acid, the gas evolved gradually becomes less pure, and especially richer in nitrous oxide*, as the amount of cupric nitrate dissolved in the liquid increases; and it was found that if cupric nitrate were added in the first instance to the acid, the amount of nitrous oxide in the gas produced was very much greater in all stages of the experiment than when the acid alone was employed. But in these experiments relatively large quantities of acid and of copper were used, and portions only of the gas evolved were collected at intervals and analysed. In order therefore, if possible, to ascertain the nature of the influence exerted by cupric nitrate, we have made several experiments in the manner already described, but dissolving nitrate in the acid before bringing the latter in contact with the metal. The results we have obtained are exhibited in Table II.

Apparently the reaction which leads to the production of the nitrous oxide does not take place to any great extent, unless a relatively large amount of the nitrate be present, or the solution be very concentrated. Thus the gas evolved by the action of 1 : 2 acid, *saturated* with cupric nitrate (Experiment XVII), contained nearly 10 per cent. of nitrous oxide and a somewhat higher proportion of nitrogen than would have been obtained in the absence of the nitrate; whereas in an experiment (XV) in which acid of the same strength but only 5 grams cupric nitrate were taken, the gas evolved contained about twice as much nitrous oxide as would have been obtained without the addition of the nitrate. Experiment XVI, in which the conditions were precisely similar to those in Experiment XV, furnished a somewhat different result; but the determination of nitrous oxide in this case was unsatisfactory, and we believe that the number given in the table is considerably too low. It should be mentioned that the copper was very much more rapidly dissolved by the saturated solution of cupric nitrate in nitric acid than by the acid alone.

The results of Experiment XIV, compared with those of Experiments III to X show, however, that the quantity of acid employed is of consequence as well as the strength of the acid, about double the proportion of nitrous oxide having been obtained when only 5 c.c, instead of the usual amount of 15 c.c. was taken. From this experiment and those with cupric nitrate it may with much probability be concluded that the extent to which the nitrate takes part in the reaction becomes greater in proportion as the amount of nitric acid

II. *Action of Copper on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				c.c. of gas calc. as NO per unit-weight of metal. Theory = 14880 c.c.
					NO.	N_2O.	N_2.*	Total.	NO.	N_2O.	N_2.	
				52·40	97·38	1·88	·74					
				41·97	96·21	3·24	·55					
				35·51	92·98	5·43	1·59					
XIV	·560	11°	{ 5 c.c. 1 : 2 }	129·88	95·79	3·28	·93	14704	14085	482	137	15926
			1 : 2 and 5 grams CuN_2O_6	41·26	91·83	5·71	2·46					
				45·56	99·50	—	·50					
XV	·4725	13°		86·82	95·85	2·71	1·44	11649	11140	314	215	12693
XVI	·1520	12°	ditto	24·36	95·76	1·09	3·15	10160	9729	111	320	11091
			1 : 2 sat. with CuN_2O_6	41·74	86·32	11·28	2·40					
				38·42	89·43	8·08	2·49					
XVII	·459	10°		80·16	87·80	9·74	2·46	11072	9721	1078	273	13505
				43·77	22·10	3·43	74·47					
			1 : 2 and 5 grams NH_4NO_3	37·39	20·80	1·93	77·27					
				26·70	64·10	—	35·90					
				6·66	12·84	—	87·15					
XVIII ...	·41	13°		114·52	30·92	1·96	67·12	17708	5475	348	11885	

diminishes, and it may be expected that results of some interest will be obtained by extending the investigation in this direction.

It certainly appeared to be somewhat remarkable, that the presence of an excess of cupric nitrate should lead to an increased production of nitrous oxide, and apparently also, though in a minor degree, of nitrogen. For a long time we were in doubt how to explain its action, until it occurred to us that probably the only way in which it could take part in the reaction would be by undergoing reduction to *cuprous* nitrate, and that the nitrous oxide was perhaps more or less directly a product of the subsequent re-oxidation of the cuprous nitrate by the nitric acid. This was the more probable as Mr. Acworth had found that the presence of potassium nitrate caused little or no alteration in the composition of the gas evolved from nitric acid and copper. In order to test the validity of our hypothesis, as cuprous nitrate was not procurable, we dissolved cuprous oxide in nitric acid, and the result obtained appears entirely to justify our assumptions. The amount of cuprous oxide taken was ·5845 of a gram, and 15 c.c. of 1 : 2 nitric acid at a temperature of 20° were employed; the oxide dissolved rapidly, and 26·19 c.c. of gas were collected without the application of heat, 11 c.c. being subsequently given off on heating, &c. The percentage composition of the two portions of gas was as follows:

$$26{\cdot}19 \text{ c.c.} \begin{cases} NO & 64{\cdot}21 \\ N_2O & 28{\cdot}32 \\ N_2 & 7{\cdot}47 \end{cases} \qquad 11{\cdot}0 \text{ c.c.} \begin{cases} 96{\cdot}06 \\ 1{\cdot}59 \\ 2{\cdot}35 \end{cases}$$

Hence the percentage composition of the total gas (37·19 c.c.) collected is

$$NO = 73{\cdot}70 \qquad N_2O = 20{\cdot}38 \qquad N_2 = 5{\cdot}92$$

and the volume obtained per unit-weight of oxide (142·8 grams)

$$NO = 6696 \text{ c.c.} \quad N_2O = 1852 \text{ c.c.} \quad N_2 = 537 \text{ c.c.} \quad \text{Total} = 9085 \text{ c.c.}$$

The evidence afforded by this experiment as compared with those in which the metal was dissolved in 1 : 2 acid is of the most definite character, and in our opinion necessitates the conclusion that the hydrogen displaced from nitric acid by copper has less reducing power than cuprous nitrate. It also renders it extremely probable, if it does not actually prove, that the nitrous oxide obtained on dissolving copper in nitric acid of various strengths is not derived from a compound or compounds formed by the reduction of a portion of the acid by the hydrogen displaced from another portion of acid by the metal, but that it is a more or less direct product of the reduction of the acid by the cuprous nitrate; in other words, we incline to the belief that, whatever the reduction-product or products may be from which the nitrous oxide is directly derived, the hydrogen displaced from nitric acid by copper has not the power of reducing nitric acid to such an extent that nitrous oxide is ultimately produced. But it will be remembered that the amount of nitrous oxide produced increases as the strength of the acid diminishes; hence, if we suppose the reduction to be effected entirely by the hydrogen displaced from the acid by the metal, the hydrogen displaced when the weaker acid is employed would appear to have a greater reducing power than that displaced when the metal is acted upon by the stronger acid, which is obviously contrary to our proposition. Not only, however, is it theoretically improbable that this should be the case, but as we shall show later on when discussing the results of our experiments with other metals, and especially with zinc, where an action similar to that which we have supposed is exerted by the cuprous nitrate is inconceivable, such a conclusion would be entirely opposed, we believe, to the evidence at our disposal. The dissolution of copper takes place, as we have already stated, with increasing slowness as the strength of the acid diminishes; a quantity of metal, for example, which is dissolved by 1 : 2 acid within 5—6 hours requiring 36—48 hours to dissolve in 1 : 8 acid; and probably this circumstance is the chief, if not the only, cause of the difference in the results observed with acids of different strengths: the explanation which we venture to advance being that a greater number of molecules of cupric nitrate come within the sphere of action of the hydrogen atoms displaced from the acid, and that consequently a greater number of molecules of cuprous nitrate are formed, when the metal slowly dissolves in weak acid than when it more rapidly dissolves in stronger acid. It may be suggested as a more probable hypothesis that the increased production of nitrous oxide is due to the presence of a relatively greater number of molecules of cupric nitrate when weak than when strong acid is used affording opportunity for a greater number of molecules of the former to undergo reduction; our observations (Experiments XV, XVI, and XVII) showing that the amount of nitrous oxide produced on dissolving copper in 1 : 2 acid in presence of an excess of cupric nitrate, *i.e.*, more than is formed from the metal itself employed in relatively small quantity, is not much increased unless a relatively very large amount of the nitrate be present, would seem, however, to negative such an assumption.

It remains only to consider the evidence afforded by our experiments with copper and nitric acid as to the manner in which the gases evolved are produced. In relation to this question the amount of gas evolved per unit-weight of metal is of especial importance. The amount of nitric oxide theoretically obtainable, supposing this gas to be derived solely from the decomposition of nitrous acid, it will be remembered is 14880 c.c. per unit-weight of metal; if the nitrous oxide be derived from the decomposition either of nitrosidic acid or of hydroxylamine nitrite (p. 57) the unit-weight of metal should furnish 5580 c.c.; and if the nitrogen result from the action of nitrous acid on ammonia at most 4464 c.c. of this gas could be evolved per unit-weight of metal dissolved. The amount of nitric oxide equivalent to the nitrous oxide produced may therefore be calculated by multiplication of the latter by 2·666, and in a similar manner by multiplying the amount of nitrogen evolved per unit-weight of metal by 3·333 we obtain the equivalent amount of nitric oxide. The results of the various experiments thus reduced are exhibited in the last column of Tables I and II. It will be seen that in the majority of cases the amount of gas obtained was below that which can be produced if the nitric and nitrous oxides and nitrogen are formed in the manner we have supposed and the decomposition be complete; and if Experiment XII be excepted, that in those cases in which the theoretical quantity is exceeded (Experiments III, IV, X, and XIV) the excess is comparatively slight. Experiment XII was one of those in which nitrous oxide was largely produced, and the result which it furnished is apparently altogether abnormal, as the amount of gas obtained (19492 c.c.) is nearly one-third in excess of the theoretical quantity. As the result of a second experiment (XIII), under what we believe to have been similar conditions was very different, it might be thought that some error had been committed in the measurement of the gas in the first experiment; but we do not think this probable, especially as the two experiments differ considerably in other respects. Thus it will be observed that in Experiment XII the last portion of gas collected, which consisted almost entirely of that given off on heating, &c., contained a very considerable proportion of nitrous oxide (21·8 per cent.), whereas in Experiment XIII the portion of gas collected in a similar manner contained very little nitrous oxide (1·57 per cent.). In other words, in the one experiment practically the whole of the nitrous oxide was evolved without the application of heat, while in the other a considerable proportion was evolved only on heating. From the observations we have made in the course of our experiments with other metals as to the manner in which nitrous oxide is evolved, we are inclined to believe that that given off in the cold and that given off on heating are products of essentially distinct reactions, and that the former is probably derived chiefly from nitrosidic acid and the latter chiefly from hydroxylamine nitrite. If this be the case, the difference in the results of the two experiments above referred to would appear to indicate that although the conditions seemingly were the same, the reduction had taken place to a greater extent in one than in the other. But this conclusion, interesting as it is in itself, in no way serves to explain the great "excess" of gas obtained in Experiment XII; in fact it must be admitted that, although the explanation we have advanced holds good in the majority of cases, especially with regard to the manner in which the nitric oxide is formed, there is in others distinct evidence of its insufficiency. It also must not be forgotten that we have determined only the gaseous products, and that, before a complete explanation of the reaction in all its phases can be given, we require, in addition to this, a knowledge of the amount of the reduction-products remaining in solution. The importance of determining these latter will be evident when it is recollected that, as we have already pointed out, a considerable quantity of nitrous acid may escape decomposition into nitric oxide, &c., and is rendered still more obvious by the fact that ammonia may be present in considerable quantity, together with nitrous acid, without much nitrogen being produced, and that therefore the amount of nitrogen obtained—supposing it all to be derived from the decomposition of ammonic nitrate—is but an imperfect measure of the amount of ammonia formed. This is shown to be the case by Experiment XVIII, Table II, where, although 5 grams of ammonium nitrate was added to the 15 c.c. of 1 : 2 acid in which the copper was dissolved, no less than 30·92 per cent. of the gas obtained consisted of nitric oxide; hence, if it be supposed that an amount of nitrous acid was formed corresponding to the quantity of copper dissolved, less the amount equivalent to the nitrous oxide produced, as much as 39·2 per cent. of the nitrous acid produced underwent the normal decomposition into nitric oxide, &c., notwithstanding the relatively very large amount of ammonium salt present. The amount of nitrogen evolved is within 428 c.c. of that which could be formed from the remaining nitrous acid, supposing that it was completely decomposed in accordance with the equation $HNO_2 + NH_3 = N_2 + 2OH_2$.

§ VI. *Action of Silver on Nitric Acid.*—The number of experiments we have made with silver is very small, but they appear to us to afford confirmation of the conclusions we have drawn from those with copper. On reference to the following table (III) it will be seen that the gas collected consisted only of nitric oxide and nitrogen; in two of the experiments, however, the amount of nitric oxide obtained was considerably less, and the amount of nitrogen considerably greater, than in the third experiment. This difference in the results is, we believe, due to the fact that in Experiment XIX the gas was pumped off immediately the metal dissolved, whereas in the two other experiments, at least twelve hours elapsed after the metal dissolved before the apparatus was exhausted, in which period a certain amount of the nitric oxide evolved during the dissolution of the metal was

III. *Action of Silver on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.			
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.
XIX ...	·4	10°	1 : 2	23·17	98·15		1·85	12511	12280		231
XX	·4	11°	1 : 2	17·78	97·18		2·82	9601	9330		271
XXI ...	·4	13°	1 : 2	17·30	96·70		3·30	9342	9033		309

absorbed by the nitric acid and reconverted into nitrous acid: $2NO + HNO_3 + OH_2 = 3HNO_2$. We may mention that the quantity of silver employed was about four hours in dissolving, and that the dissolution proceeded more and more rapidly as the amount of nitrous acid in solution became greater, which is in accordance with the observations of **Russell** and others. In Experiment XIX about half the gas was given off previous to heating; while in Experiment XX, of the 17·78 c.c. of gas obtained, 9·5 c.c. were evolved in the cold; and in Experiment XXI, only 5·92 c.c. were collected before heating, and 11·38 c.c. after heating several times. The gas collected after heating in Experiments XX and XXI contained about the same proportion of nitrogen as that collected in a similar manner in Experiment XIX, and as the apparatus employed was that provided with a caoutchouc plug, it is highly probable that the increased amount of nitrogen obtained in Experiments XX and XXI was due to leakage; we are, in fact, almost inclined to regard the whole of the nitrogen obtained in these experiments as derived from external sources, rather than as the product of the action of the silver on the acid, the amount actually collected in Experiment XIX being only ·43 c.c., a quantity which is easily accounted for when it is remembered that the exhaustion of the air from the apparatus is necessarily incomplete in the first instance, and that even if actual leakage does not occur at any of the joints, there is undoubtedly a slow diffusion of air through the caoutchouc plug.

The non-production of nitrous oxide affords strong evidence in favour of the explanation we have advanced of the manner in which this gas is formed when copper is dissolved in nitric acid, for there is no probability in the case of silver that a reaction can take place corresponding to the reduction of cupric to cuprous nitrate; and from its general behaviour, and especially from **Thomsen's** thermochemical investigations (*J. pr. Chem.* [2], xii, 271), there is every reason to believe that the energy of silver is much below that of copper; consequently if the hydrogen displaced from nitric acid by copper be incapable, as we have suggested, of directly reducing nitric acid to the extent sufficient for the production of nitrous oxide, it is extremely improbable that the hydrogen displaced by silver should have this power, which is in accordance with our observations.

§ VII. *Action of Zinc on Nitric Acid.*—The results of our experiments with zinc are exhibited in Table IV, from which it will be seen that whatever the strength of the acid, the gas evolved is always a mixture of nitric oxide, nitrous oxide, and nitrogen. As in the experiments with copper, the amount of nitric oxide evolved per unit-weight of metal varies not only with acid of different strengths, but also with acid of the same strength; probably, however, this is at least in part due to the difficulty with which, as we have before pointed out, the nitrous acid produced is entirely decomposed, especially in presence of concentrated nitric acid.

In our opinion the most important element for consideration in the case of the metal under discussion is the amount of nitrous oxide produced, as this probably corresponds strictly with the amount of nitrosidic acid and of hydroxylamine—supposing these to be the two bodies from which the nitrous oxide is more or less directly derived—formed in the reaction: the decomposition of the former into nitrous oxide and water being doubtless immediate, while the production of nitrous oxide by the action of nitrous oxide on the latter, according to V. Meyer's observations (*Ann. Chem. Pharm.*, clxxv, 141), takes place with great facility.

Now it will be observed that the amount of nitrous oxide evolved on dissolving the metal in acid varying in strength from 1 : 8 to 1 : 2 at the ordinary temperature, that is to say, in Experiments XXII to XXXII inclusive, but excluding Experiment XXIX, is on the whole remarkably constant, the lowest amount being 2422 c.c. (Experiment XXVIII), and the highest 2862 c.c. (Experiment XXII); and as there is no great variation in the amount of nitrogen, these results would appear to indicate that within the specified limits of concentration the extent to which the various reactions take place is influenced in a comparatively slight degree by alterations in the concentration of the acid. From the increased amount of nitrogen produced in Experiments XXXV and XXXVI, it would almost appear that considerably more ammonia had been produced than in the experiments with weaker acid. This explanation is not a necessary one, however, as another explanation may be given of the increase in the amount of nitrogen. Thus we have already pointed out that the amount of nitrogen evolved is but an imperfect measure of the amount of ammonia formed in the reaction, as a considerable proportion of the nitrous acid fails to act on the ammonia present, even if the latter be in great

IV. *Action of Zinc on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
XXII	·4	5°	1 : 8	35 ·33	46 ·05	49 ·86	4 ·09	5741	2643	2862	236	74 ·33
XXIII....	·4	6°	1 : 8	35 ·80	47 ·95	48 ·08	3 ·97	5817	2789	2797	231	74 ·03
XXIV....	·4	6°	1 : 4	37 ·52	53 ·45	43 ·35	3 ·24	6097	3258	2643	196	73 ·64
XXV	·4	8°	1 : 4	35 ·33	49 ·34	46 ·10	4 ·56	5741	2832	2646	263	72 ·33
XXVI....	·4	5°	1 : 4	34 ·39	49 ·08	47 ·60	3 ·32	5588	2742	2659	187	70 ·25
XXVII ..	·415	7°	1 : 4	34 ·87	46 ·71	50 ·30	2 ·99	5461	2550	2748	163	70 ·02
XXVIII..	·226	6°	1 : 4	15 ·80	38 ·08	53 ·30	8 ·62	4544	1730	2422	392	63 ·80
XXIX ...	·283	90°	1 : 4	25 ·17	57 ·44	35 ·20	7 ·36	5781	3320	2034	427	68 ·32
XXX	·4	7°	1 : 2	31 ·30	45 ·30	49 ·90	4 ·80	5086	2304	2538	244	65 ·77
XXXI ...	·4	8°	1 : 2	31 ·63	47 ·75	48 ·08	4 ·17	5140	2454	2471	215	65 ·58
				23 ·73	33 ·52	60 ·17	6 ·31					
				4 ·06	84 ·27	5 ·95	9 ·78					
XXXII ..	·386	12°	1 : 2	27 ·79	40 ·91	52 ·21	6 ·88	4679	1914	2442	323	63 ·85
				47 ·64	22 ·62	70 ·79	6 ·59					
				40 ·68	18 ·00	73 ·78	8 ·22					
				14 ·52	32 ·27	61 ·23	6 ·50					
				7 ·64	72 ·14	19 ·54	8 ·32					
XXIII ...	1·6	10°	1 : 2	110 ·48	25 ·59	67 ·08	7 ·33	4488	1148	3010	330	68 ·88
XXXIV..	·221	90°	1 : 2	19 ·31	51 ·88	39 ·99	8 ·13	5679	2946	2271	462	70 ·83

V. *Action of Zinc on Nitric Acid*—continued.

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
				19·62	24·70	66·66	8·64					
				2·76	77·84	8·88	13·28					
XXXV ..	·3455	15°	1 : 1	22·38	31·23	59·56	9·21	4210	1314	2507	389	62·46
XXXVI ..	·321	15°	1 : 0	15·68	·95	78·29	20·76	3175	31	2485	659	59·49
XXXVII.	·4	6°	1 : 4 and 5 grams NH_4NO_3	41·43	41·98	37·48	20·54	6732	2826	2523	1383	95·18
XXXVIII.	·242	6°	ditto	21·16	41·59	41·25	17·16	5928	2466	2445	1017	83·16
				39·00	—	3·69	96·31					
			sat. sol. NH_4NO_3	9·35	—	—	100·00					
XL	·179	12°		48·35	—	2·97	97·03	17557	—	521	17036	85·64

excess; that this is the case is further proved by Experiments XXXVII and XXXVIII, where, notwithstanding 5 grams of ammonium nitrate were added, as much nitric oxide was obtained as in many of the experiments in which no such addition was made. But as the amount of nitrous acid escaping decomposition into nitric oxide, &c., is greater the more concentrated the acid, we may expect that if a greater amount of nitrous acid remain in solution, or, indeed, if it undergo dissociation more slowly when concentrated than when dilute acid is employed, the amount of nitrogen evolved will be greater in the former than in the latter case, even supposing the amount of ammonia present in both cases to be the same.

In Experiments XXIX and XXXIV, in which the acid was heated to about 90° before dropping in the metal, considerably more nitrogen was obtained than in corresponding experiments in which the acid was not thus heated.* A somewhat similar explanation as the above may be advanced in regard to these results, for supposing the same amounts of ammonia and of nitrous acid to be formed under the two sets of conditions, it is probable that more of the ammonia would suffer decomposition by the nitrous acid at the higher temperature.

We are not, however, at all inclined to regard this explanation as sufficient, but believe that our experiments rather justify the conclusion that reduction does take place to a greater extent and proceed further the more concentrated the acid and the higher the temperature. Still this is but a mere opinion, and must remain such until not only the gaseous products, but also those which remain in solution in the acid, shall have been determined.

The last experiment with zinc and nitric acid to which we have to direct attention is that numbered XXXIII, where the amount of metal dissolved was four times as great as in the other experiments under otherwise similar conditions. It will be observed that in this case considerably less nitric oxide and considerably more nitrous oxide was obtained than in any of the experiments with smaller quantities of metal. This probably is due to the fact that when a larger quantity of metal is employed, there is a greater opportunity for the nitrous acid produced by the action of the first portions of metal dissolved to undergo reduction side by side with the nitric acid. It is worthy of note, however, that this "division of labour," so to speak, cannot take place with all metals, for in the case of silver no nitrous oxide is produced, notwithstanding the extreme slowness with which the metal dissolves, and the richness of the solution after a time in nitrous acid.

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* Even when cold acid was employed, the metal (very thin foil) dissolved with great rapidity, much heat being developed, so that the mean temperature at which the dissolution of the metal was effected was considerably higher than that of the acid at the commencement of the experiment.

Probably the extent to which nitric and nitrous acids undergo reduction when simultaneously present will be found to be a function of the "energy" of the hydrogen displaced by the action of the metal.

In the Table of Results, on p. 75, an experiment with zinc and ammonium nitrate solution is included which may here be briefly mentioned. Zinc dissolves readily in a concentrated solution of this salt, especially if ammonia be added, much heat being developed; if a moderate amount of metal be taken, and the solution be carefully cooled, no gas is evolved; but on heating the solution a mixture of nitrous oxide and nitrogen is given off, the former increasing in amount with the quantity of metal dissolved. When, after repeated heating, gas is no longer given off, the whole of the nitrite and (?) nitroside appears to have been decomposed, as the solution is immediately coloured by permanganate, even when acidulated, and as the whole of the metal is not accounted for in the form of these gases, it is probable that ammonia is also produced. It is proposed to extend these experiments, and also to observe the action of other metals on ammonium nitrate as well as on other nitrates.

It should here be stated that M. Saint-Claire Deville has published a most valuable account of a number of experiments on the action of zinc on very dilute solutions of nitric acid (solutions containing an amount of acid corresponding to from 2 to 20 grams of the anhydride per litre), and also on mixtures of nitric and hydrochloric acids and of nitric and sulphuric acids (De l'état naissant, *Compt. rend.*, 1870, lxx, 22, 550). M. Deville, however, appears to regard the various products as formed from the acid by the direct action of the metal, a view which is in opposition to our own. One of us proposes to discuss this subject on a future occasion.

§ VIII. *Action of Cadmium and Magnesium on Nitric Acid.*—The results of our experiments with these metals are exhibited in Tables V and VI. It will be observed that with cadmium considerably more nitric oxide and less nitrous oxide was obtained than on dissolving zinc in acid of the same strength. There is a considerable difference between the two experiments in the amounts of nitrogen produced, but it will be noticed that less nitrous oxide and more nitric oxide was obtained in that which yielded the larger amount of nitrogen, and it is possible, therefore, that the reduction had proceeded further in this case. The difference may be at least in part due to the fact that a larger amount of the metal was employed in the second experiment.

The behaviour of magnesium as compared with that of cadmium and zinc presents several points of interest. Much less nitric oxide was obtained with this metal than with either of the latter, neither of which, however, furnished so large an amount of nitrous oxide; and

V. *Action of Cadmium on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
				21·14	67·53	28·53	3·94					
				13·91	96·51	1·38	2·11					
XLI......	·3655	13°	1 : 2	35·05	79·00	17·74	3·26	10740	8485	1905	350	98·99
				28·13	72·27	25·88	1·85					
				9·00	96·95	2·45	·60					
XLII	·416	11°	1 : 2	37·13	78·21	20·17	1·62	9996	7818	2015	163	92·30

VI. *Action of Magnesium on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
				47·22	6·37	69·22	24·41					
				13·82	26·40	59·31	14·29					
				6·77	79·94	12·87	7·19					
XLIII....	·3085	12°	1 : 2	67·81	17·87	61·55	20·58	5275	944	3246	1085	88·81
				40·52	10·94	62·10	26·96					
				25·34	21·28	57·32	21·40					
				3·84	74·65	5·70	19·65					
XLIV....	·314	13°	1 : 2	69·70	17·38	58·09	24·53	5327	926	3094	1307	90·93

the amount of nitrogen produced is far in excess of that obtained with either zinc or cadmium; and there can therefore be little doubt that magnesium is a far more "active" metal than either zinc or cadmium; but the production of so large an amount of nitrogen appears somewhat remarkable, and tends perhaps to throw some doubt on the sufficiency of our explanation of the mode of formation of the nitrogen, as certain of our experiments with zinc (XXXVII and XXXVIII) show that the influence exercised even by a relatively very large quantity of an ammonium salt in increasing the production of nitrogen is by no means great.

As with cadmium, there is a noticeable difference between the amounts of nitrous oxide and nitrogen obtained in the two experiments; and in the case of both metals the lesser quantity of nitrous oxide corresponds with the greater quantity of nitrogen, a lower percentage of metal also being accounted for in the experiments which yield the smaller quantity of nitrogen. This may be in part due to the fact that the heating, &c., was more often repeated in the one case than in the other. There is, however, internal evidence, especially in the case of magnesium, tending to show that this explanation is insufficient; for it will be observed that in the one experiment with this metal the portion of gas last collected—that given off entirely on heating—was far richer in nitrous oxide and poorer in nitrogen than in the other. A similar difference may be observed on comparing the results of two of the experiments with zinc (XXXII and XXXIII). Thus the gas given off on heating contained in the one case only 5·95 per cent. of nitrous oxide, but in the other no less than 19·54 per cent., the only difference between the two experiments being that the amounts of metal taken were not the same (·386 and 1·6 grams). The results of the two experiments with cadmium also differ in a similar but much less marked manner. If, as we have previously suggested, the decomposition of nitrosidic acid into nitrous oxide and water is immediate, and the nitrous oxide given off on heating is due to the decomposition of hydroxylamine, the differences here referred to indicate apparently that the extent to which the various reactions take place may be considerably affected by what seem to be very slight alterations in the conditions of experiment.

Lastly we may point out as noteworthy that the percentage of metal accounted for in the form of gaseous products is far higher with both cadmium and magnesium than with zinc. It is scarcely possible at present to give any satisfactory explanation of this, especially as zinc would appear to be intermediate in its properties between cadmium and magnesium.

§ IX. *Action of Iron on Nitric Acid.*—The gases obtained on dis-

VII. *Action of Iron on Nitric Acid.*

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
				40·79	95·77	1·71	2·52					
				13·43	79·29	—	20·71					
XLV.....	·251	16°	1 : 1	54·22	91·68	1·28	7·04	8064	7392	104	567	64·23
				35·70	83·35	11·21	5·44					
				20·38	97·49	·30	2·48					
				7·78	90·74	—	9·26					
XLVI....	·3975	13°	1 : 2	63·86	88·77	6·26	4·97	5997	5323	375	299	49·18
				41·33	83·24	12·17	4·59					
				6·58	93·76	4·80	1·44					
				9·21	94·52	1·48	4·00					
XLVII...	·400	10°	1 : 4	57·12	86·27	9·59	4·14	5330	4598	551	221	45·72
				46·98	86·11	10·29	3·60					
				8·41	95·37	1·98	2·65					
XLVIII..	·379	13°	1 : 4	55·39	87·50	9·02	3·48	5456	4773	492	191	45·15
				34·45	92·36	4·58	3·06					
				15·85	97·15	·99	1·86					
XLIX....	·318	12°	1 : 8	50·30	93·87	3·43	2·70	5904	5542	202	160	44·44
L........	·200	9°	1 : 12	30·81	91·28	4·45	4·27	5638	5146	252	242	44·51

solving this metal* in nitric acid, &c., consist chiefly of nitric oxide, the amounts of nitrous oxide and nitrogen evolved being relatively small. It will be observed, however, that as the concentration of the acid diminishes, the amount of nitrous oxide produced per unit-weight of metal (two-thirds of 56 grams) at first increases and afterwards diminishes; whereas the nitric oxide at first considerably diminishes in amount as the concentration of the acid sinks, but at a certain point increases as the concentration is still further reduced.

These differences in the amounts of nitric and nitrous oxides evolved with different strengths of acid, correspond with perceptible differences in the behaviour of the metal during dissolution. In 1 : 1 and 1 : 2 acid the iron dissolves very rapidly, producing a pale greenish-yellow coloured liquid; in 1 : 4 acid, however, it dissolves somewhat less rapidly, and the solution is of a dark brown colour, as also is that produced on dissolving in 1 : 8 and 1 : 12 acid, which, the latter especially, act upon it still more slowly. From this there can be no doubt that by the action of the more concentrated acid the iron is immediately converted into ferric salt, whereas when weaker acid is employed ferrous salt is first formed, and is converted into ferric salt only on afterwards heating the liquid;† and it would appear probable that the hydrogen displaced in the formation of the ferrous salt is more "active" than that displaced in the formation of the ferric salt.

The manner in which the nitrous oxide is evolved appears also to indicate that the hydrogen displaced from weaker solutions of nitric acid is more active in effecting reduction. Thus it will be noticed that in Experiment XLVI, with 1 : 1 acid, the last portion of gas collected—that evolved on heating—is free from nitrous oxide, which is also the case in Experiment XLVII with 1 : 2 acid; in this latter experiment, moreover, the second portion of gas collected—that extracted by continuing the action of the pump after practically the whole of the gas evolved during the dissolution of the metal had been removed from the apparatus—is almost free from nitrous oxide. A second experiment with 1 : 2 acid, not quoted here, gave precisely similar results. In the case of the weaker acid, however, the gas evolved on heating contains a considerable proportion of nitrous oxide, which, as we have before suggested, is probably derived from the decomposition of hydroxylamine, whilst that immediately evolved without the application of heat is probably in great part, if not entirely, the product of the decomposition of nitrosidic acid.

§ X. *Action of Nickel, Cobalt, Indium, and Aluminium on Nitric Acid.*

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* The iron employed was a portion of the pure iron prepared by the late Dr. Matthiesen, for which we are indebted to Dr. Russell, F.R.S.

† A mixture of ferrous and ferric salt is doubtless produced with certain strengths of acid, in proportions varying with the concentration of the acid.

—The results obtained with these metals are represented in Table VIII; although few in number, they appear to us to possess very considerable interest.

Nickel.—This metal would seem to be far more "active" than iron, as it yields a much smaller amount of nitric oxide, and a considerably larger amount of nitrous oxide; the low percentage of metal accounted for is probably to be regarded as evidence of the production of a considerable amount of ammonia, and affords additional proof of the "activity" of nickel. The amounts of nitric and nitrous oxides produced in the two experiments differ considerably, but different amounts of metal were dissolved, and here again it will be noticed that the lesser amount of nitric oxide and the greater amount of nitrous oxide is obtained from the larger amount of metal, which may be accounted for, as we have before said, if we suppose that the nitrous acid produced in the first instance undergoes reduction side by side with the nitric acid. Nickel, at least in the form in which we have employed it,* dissolves with extreme slowness in nitric acid, the time occupied in effecting the dissolution of the quantities taken in Experiments LI and LII having been upwards of 50 and 70 hours respectively.

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* I am indebted to Dr. Russell for the nickel and cobalt used in these experiments. They were portions of the pure metals prepared for his researches on the atomic weights of these elements (this Journal, xvi, 51; xxii, 294). The nickel was in the form of hard, dull greyish lumps. On analyzing the gaseous mixture evolved on dissolving it in nitric acid, it was found to contain hydrogen, of which 1·47 c.c. was obtained in Expt. LI, and 2·28 c.c. in Expt. LII, or 625 c.c. and 617 c.c. respectively from 100 grams of nickel. As in the course of this investigation the production of hydrogen has never been observed on dissolving metals in 1 : 2 acid, or indeed in nitric acid of any strength, and as moreover no hydrogen was obtained on dissolving fused commercial nickel (Expt. LIII), there can be no doubt that the hydrogen had been occluded by the metal during its preparation from the oxide by reduction in hydrogen. This fact that occluded hydrogen is without action on nitric acid is, however, of very considerable interest, as it may be possible by the action of nitric acid to ascertain whether, as has been suggested, a portion of the hydrogen occluded by palladium is combined with the metal. I also propose to apply the method to the study of the gases in meteorites, and it may here be remarked that this discovery of the power of nickel to occlude a very considerable volume of hydrogen explains the occurrence of such large amounts of this gas in meteorites which previously on account of the slight power of occluding hydrogen which iron alone appeared to possess, was somewhat difficult of explanation.

No hydrogen was obtained from the cobalt, although it had also been prepared from the oxide by reduction in hydrogen. But the piece dissolved was the only one in the bottle from which it was taken preserving a metallic appearance: the remainder of the specimen had assumed a brown friable condition, having evidently undergone oxidation. I am inclined to believe from this that the cobalt had originally been charged with hydrogen, with the exception of the piece used by us, which was extremely dense and compact. The spontaneous oxidation of metals prepared by reduction in hydrogen is, in fact, very probably always due to the presence of occluded hydrogen.—H. E. A.

VIII.

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
					Nickel.							
LI	·2355	13°						·93	·04	·612	219	34·52
LII	·3695	15°						[illegible]	58	·869	200	38·36
LIII		11°								—	—	—
					Cobalt.							
LIV		18°	2		5·71	79·23				863	164	19·55
					Indium							
LV			2		90·57	4·49				376	416	67·13
					Aluminiu							
LVI					97·0	·7	2·3					

Cobalt.—This metal, like nickel, dissolves with extreme slowness in 1 : 2 acid. From the one experiment we have made it would appear to be as much superior in "activity" to the allied metal nickel as this latter is to iron.

Indium.—A small quantity of this metal was kindly presented to us by Dr. Gladstone, F.R.S. It is acted upon with extreme slowness by 1 : 2 acid, the time occupied in dissolving the ·265 gram employed in the experiment, of which the results are exhibited in Table VIII, having been upwards of 70 hours. It appears to be possessed of considerable "activity," as from the comparatively low percentage of metal accounted for, and the comparatively large amount of nitrogen obtained, it is probable that a considerable amount of ammonia is formed.

Aluminium.—This metal was so slowly acted upon at the ordinary temperature, that we found it necessary to heat the acid to about 60°—65°, when it dissolved with moderate rapidity. It appears to resemble silver in its action on nitric acid, and most probably it furnishes only nitric oxide.

§ XI. *Action of Tin, Lead, and Thallium on Nitric Acid.*—The results of our experiments with these three metals are given in Table IX.

Tin.—In the experiments with 1 : 0 and 1 : 1 acid, white (?) metastannic acid separated out as the metal dissolved, but in the remaining experiments clear solutions were obtained, from which no separation took place until they were heated, when, however, the liquid became almost semi-solid. It will be observed that not only the nitric oxide, but also the nitrous oxide and nitrogen increase in amount, and then diminish as the concentration of the acid diminishes, and it is probable, therefore, that, as in the case of iron, there is a difference in the "activity" of the hydrogen, according as the product is a stannic or a stannous salt.

Judging from the composition of the gaseous mixture, and the quantities of gas obtained before and after heating, when 1 : 2 acid is employed (Experiment LIX), it appears probable that in the dissolution of the metal to (?) stannous salt, a relatively small amount of nitrous acid, but considerable amounts of nitrosidic acid and ammonia are produced; and that in the conversion of the stannous into stannic salt, which takes place on heating, chiefly those reactions occur which lead to the production of nitrous oxide.

Lead.—The most noticeable feature with regard to the action of this metal on nitric acid is that comparatively large amounts of nitrous oxide and nitrogen are produced, and as a very considerable proportion of the metal is unaccounted for, it is very probable that much ammonia

IX.

No. of expt.	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
						Tin.						
LVII	·4135	14°	1 : 0	21·54	1·08	85·14	13·78	3073	34	2616	423	56·58
LVIII ...	·414	15°	1 : 1	31·02	16·38	73·82	9·80	4420	724	3263	433	73·03
				5·32	2·57	79·17	18·26					
				29·85	25·93	65·77	8·30					
LIX......	·404	11°	1 : 2	35·17	22·37	67·78	9·85	5136	1148	3481	506	81·20
LX	·4145	12°	1 : 2	33·09	14·47	75·55	9·98	4710	781	3558	470	79·52
LXI	·415	11°	1 : 8	4·66	3·27	85·02	11·80	3312	106	2816	390	71·76
						Lead.						
LXII	·381	14°	1 : 2	10·56	51·23	41·47	7·30	5737	2939	2379	419	71·76
				5·06	2·45	81·90	15·65					
				4·82	54·85	41·89	3·26					
LXIII....	·403	11°	1 : 2	9·88	28·06	62·37	9·57	5074	1423	3164	487	77·16
						Thallium.						
				2·38	34·92	38·66	26·42					
				4·04	90·38	7·72	1·90					
LXIV	·3065	30°	1 : 2	6·42	69·78	19·15	11·07	8546	5963	1636	947	90·59

remains in solution. From the composition of the gases collected before and after heating (Experiment LXIII), it would seem that much of the nitrous oxide is derived from the decomposition of hydroxylamine.

Thallium.—Although much more nitric oxide, and considerably less nitrous oxide is furnished by this metal than by lead, the amount of nitrogen produced is much greater; but as the percentage of metal accounted for is high, the results we have obtained do not appear to warrant the conclusion that thallium is a more "active" metal than lead in respect of its action on nitric acid.

§ XII. *Action of Alloys on Nitric Acid.*—As yet we have only submitted two alloys to examination, viz., brass and gun metal; the results obtained are exhibited in Table X.

X.

	Weight of metal taken.	T.	Strength of acid used.	c.c. of gas obtained.	Percentage composition of gas.			c.c. of gas per unit-weight of metal.				Per cent. of metal accounted for.
					NO.	N_2O.	N_2.	Total.	NO.	N_2O.	N_2.	
Brass	·374	15°	1 : 2	75·35	97·02	1·64	1·34	12773	12392	210	171	90·74
				21·82	35·70	57·26	7·04					
				23·37	86·46	9·23	4·31					
Gun metal.	·317	16°	1 : 2	45·19	61·93	32·41	5·66	9038	5597	2929	512	101·57

Our object in making these experiments was, if possible, to throw further light on, and to obtain some explanation of, the differences observed in the behaviour of various metals towards nitric acid. Thermochemical investigation has shown that, as a general rule, a considerably greater amount of heat is developed in the formation of the magnesium compounds than in the formation of the corresponding compounds of either zinc or cadmium, and more in the formation of those of zinc than of those of cadmium; and as from the composition of the gases obtained on dissolving these metals in nitric acid it would appear that the first-mentioned is the most, and the last-mentioned the least "active," we are inclined to believe that the extent to which reduction takes place on dissolving a given metal in nitric acid is a function of the energy developed in the reaction, $R'_n + nHNO_3 \pm Aq = nR'NO_3 \pm Aq + nH$, *i.e.*, in the displacement of the hydrogen of the acid by the metal, including that developed subsequently by the action of the water present on the salt which is produced. This, however, we regard at present merely as a working hypothesis, for it must not be forgotten that we have not yet sufficient data to enable us to decide absolutely as to which of two related metals is possessed of the greater "activity," inasmuch as only the gaseous products of reduction have been determined; this being the case even with regard to magnesium and zinc, as although less nitric oxide, and considerably larger quantities of nitrous oxide and nitrogen are furnished by magnesium than by zinc, the percentage of metal accounted for in the form of gaseous products is considerably less in the case of the latter. Moreover, in many instances, at least, reaction takes place not only between the metal and nitric acid, but also between the former and the nitrous acid, which is the first product of reduction of the latter; and that this may have an important influence on the final result, and may much complicate the discussion of the phenomena concerned, is evident from the fact that platinum, for example, will dissolve in nitrous, but not in nitric acid, and that silver, if not insoluble in nitric acid, is certainly much more readily dissolved by nitrous acid. It will be remembered also that the amount of metal employed is not always without influence on the result, and that we have suggested that this is a consequence of the accumulation of nitrous acid in the solution.

Roscoe, however, has shown that zinc and cadmium are considerably more "active" than magnesium in reducing the vanadic compounds, a solution of the pentoxide in sulphuric acid being reduced to a salt of the tetroxide by sulphurous acid and hydrogen sulphide; to a salt of the trioxide by magnesium; and to a salt of the dioxide by zinc, cadmium, and sodium amalgam; and it may be said that these observations are in opposition to our conclusions as to the relative "activity" of magnesium, zinc, and cadmium. But the discussion of the phenomena involved in these changes is doubtless also complicated by the occurrence of a series of reactions; so that, in fact, until we are acquainted with the entire series, and are able to deduce the dynamic values corresponding to the several reactions, we must refrain from drawing conclusions as to the reason of the superior activity of zinc and cadmium in reducing vanadium pentoxide, and of the superiority of magnesium in reducing nitric acid.

Moreover, if the activity of a given metal depend, as we suppose, on the amount of "available" energy associated with the hydrogen displaced by the metal from the acid, our present knowledge would lead us to expect that the same metal may produce very different results with different acids, for the reason that probably not only are different amounts of heat developed by the mere displacement of the hydrogen in different acids by the same metal, but the compounds formed by the displacement of the hydrogen of the acid by the metal doubtless enter into reaction with the water present, and in other ways, and probably very different amounts of heat are developed in these reactions by different salts of the same metal. For the same reason we may expect also that alterations in the conditions of experiment, viz., in the degree of concentration of the acid and of the temperature at which the metal is dissolved, will perceptibly influence the result in many cases. The rapidity with which the metal dissolves may also influence the result; there can be little doubt of this in the case of copper, as we have pointed out, and Deville has shown (*Compt. rend.*, lxx, 20, 550) that a relatively much larger amount of nitric acid is required to prevent the evolution of hydrogen when zinc is dissolved in a mixture of nitric and hydrochloric acids than when it is dissolved in a mixture of nitric and sulphuric acids, a result which he attributes in great measure to the fact that the zinc is dissolved more rapidly by the hydrochloric than by the sulphuric acid.

It is well known that in the formation of many alloys from their constituent metals, much heat is developed. From this it follows that the energy of the associated metals must be reduced, and it appeared to us that if our hypothesis above stated were correct, the comparison of the behaviour of a given alloy with that of its constituent metals towards nitric acid should afford evidence of this: that, in fact, reduction of the acid would take place to a less extent on dissolving a given amount of the alloy than on dissolving corresponding amounts of its constituent metals. Only two experiments have as yet been made, one with brass, and the other with gun metal. The brass employed contained 30·2 per cent. zinc, 69·1 per cent. copper, and ·7 per cent. lead and tin; the gun metal 10·90 per cent. tin, 88·5 per cent. copper, and a little lead.

It will be seen on reference to the table, that the brass behaves exactly as copper, the percentage of nitrous oxide and nitrogen being no greater than with copper, and the amount of nitric oxide per unit-weight of metal (regarded as copper) is as high as was obtained in most of the experiments with copper alone under similar conditions. So far as its behaviour towards nitric acid is concerned, the zinc may indeed be said truly to have undergone transmutation into copper, and this result appears to us to afford much support to the hypothesis we have advanced in explanation of the difference in the behaviour of different metals.

The result obtained with gun metal is more difficult of interpretation; it would seem, however, from the large amount of nitrous oxide produced, and the manner in which it is evolved—chiefly in the cold—that whilst the "activity" of the tin is reduced by its association with copper, that of the copper on the other hand, is considerably raised by its association with tin; but whether the gain to the copper is less than the loss to the tin it is impossible to decide from this one experiment.

A most interesting series of observations on the action of acids on alloys of zinc and copper, and of tin and copper, in various proportions, were published some years ago in this Journal by Messrs. Calvert and Johnson (1866, xix, 434), which appear to us further to support our hypothesis. The method they adopted was to determine the loss experienced in a given time by a given surface of the alloy exposed to the action of a given quantity of the acid at a known temperature, and the results obtained in this way indicate that the influence of a metal such as copper, in reducing the "activity" of metals such as zinc and tin, is very considerable. Thus, whereas an alloy of zinc and copper containing 67·26 per cent. of zinc and 32·74 per cent. of copper, lost 2550 grams per square metre of surface, when exposed to the action of nitric acid of sp. gr. 1·10, an alloy containing 50·95 per cent. of zinc and 49·05 per cent. of copper lost only 45 grams per square metre of surface; and the loss experienced by alloys still richer in copper was even less. Again, whereas an alloy of tin and copper, in the proportion corresponding to the formula Sn_5Cu, containing 90·27 per cent. of tin and 9·73 per cent. of copper, lost 1883 grams per square metre when exposed to the action of nitric acid of sp. gr. 1·25, the alloy represented by the formula $SnCu$, containing 65·02 per cent. of tin and 34·98 per cent. of copper, lost only 183 grams per square metre; alloys containing a larger proportion of copper were found to be somewhat more acted upon, that of the formula $SnCu_5$ losing 808 grams per square metre.

Although much important information has been gained as to the behaviour of a large number of the metals with nitric acid, the results narrated in the previous pages are chiefly of value as indicating the directions in which the investigation must be continued in order to obtain the requisite data for the complete discussion of the problem under consideration.

In the first place it will be necessary to study the action upon each other in presence of nitric acid of all the possible reduction products—nitrous acid, nitrosidic acid, hydroxylamine, ammonia—under conditions as similar as possible to those which obtain when the metals are dissolved in nitric acid. Then the action of metals on nitric acid must be again submitted to examination, and both the gaseous products and those remaining in solution determined; and as very slight variations in the conditions of experiment often appear to exert an appreciable influence on the final result, it will be necessary to determine the two series of products wherever possible in one and the same experiment.

In the case of those metals which furnish two series of salts, it will be requisite to examine separately the action of the *ous* salts—of the ferrous and stannous salts, for example, as these may behave very differently from the metals themselves. Lastly, a series of experiments on the action of various metals on the same mixture of nitric and hydrochloric or sulphuric acids will doubtless throw much light on the question of the difference in behaviour of the different metals.

I hope very shortly to be able to give an account to the Society of the results obtained in continuation of this investigation.—H. E. A.

IX.—*On Dibromacetic and Glyoxylic Acids.*

By W. H. PERKIN, F.R.S.

SEVERAL years since (*Journ. Chem. Soc.*, xi, 22), in conjunction with the late Mr. Duppa, I gave an account of bromo- and dibromo-acetic acids and some of their derivatives; amongst these were the products obtained by the decomposition of their silver salts when heated with water, that of the former acid yielding silver bromide and glycollic acid, that of the latter silver bromide and an acid which we believed to be bromo-glycollic acid.

Our reasons for believing this to be bromoglycollic acid were various; one was from the apparent analogy of the reaction by which it is formed from silver dibromacetate, to that by which glycollic acid is produced from silver bromacetate, thus—

$$\underset{\text{Silver bromacetate.}}{C_2H_2BrAgO_2} + OH_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3} + AgBr.$$

$$\underset{\text{Silver dibromacetate.}}{C_2HBr_2AgO_2} + OH_2 = \underset{\text{Bromoglycollic acid.}}{C_2H_3BrO_3} + AgBr.$$

A second reason was because its silver salt when boiled with water yielded silver bromide and glyoxylic acid apparently, thus—

$$\underset{\text{Silver bromoglycollate.}}{C_2H_2BrAgO_3} + H_2O = \underset{\text{Glyoxylic acid.}}{C_2H_4O_4} + AgBr.$$

From the difficulty of preparing dibromacetic acid in large quantities at that time, we were prevented from investigating this matter very fully; nor did we consider it important to do so, as we had no reason to doubt the correctness of the conclusions we had arrived at.

Since then new processes for the preparation of bromo- and dibromacetic acids have been discovered, by which they can be obtained more easily; I therefore thought it would be interesting to make a more complete examination of this so-called bromoglycollic acid.

The process adopted for the preparation of dibromacetic acid consisted simply in the use of acetic anhydride in the place of glacial acetic acid for the production of the bromacetic acid required; the anhydride being readily acted upon by bromine, the use of sealed tubes is thus avoided. The bromacetic acid so obtained was converted into the dibromo acid by treatment with bromine in sunshine whilst heated to its boiling point as previously described. Considerable quantities were thus prepared, and the acid was usually in the crystalline state. A portion converted into the silver salt gave the following results on analysis:—

·6695 of substance gave
·3833 of AgBr = 32·87 p. c. Ag.

Theory for $C_2HBr_2AgO_2$ requires 33·23 p. c. Ag.

Decomposition of Silver Dibromacetate when heated with Water.

Having obtained a supply of dibromacetic acid, a considerable quantity of its silver salt was prepared, and a portion of it boiled with water until silver bromide ceased to be formed. The decomposition takes place with considerable energy when quantities of about 20 grams of silver salt are used, the ebullition continuing for some time after the removal of the source of heat. The resulting dilute acid liquid was separated from silver bromide by filtration, concentrated over the water-bath, nearly neutralised with sodium carbonate, and converted into the silver salt by precipitation with silver nitrate. It was then washed and dried in a vacuum. A silver determination gave the following numbers:—

·2447 of substance gave
·177 of silver bromide = 41·55 p. c. Ag.

The calculated percentage for silver bromoglycollate, $C_2H_2BrAgO_3$, is 41·22 p. c. Ag.

This result appeared to confirm the correctness of the equation already given; but by experimenting under different conditions very variable results were obtained. For example, when dilute solutions of the acid product obtained by boiling silver dibromacetate with water were used for the preparation of a silver salt, the resulting compound always contained a smaller percentage of silver than when strong and neutralised ones were employed.

To get a clue to this unexpected result fractional precipitation was resorted to, which soon showed that the product was not a definite body, but a mixture, the first crops giving low, and the last ones high percentages of silver. The following is an example selected from several experiments:—

First crop contained 33·06 p. c. silver.
Third „ 45·86 „

It was soon remarked that the first crops often gave percentages of silver closely corresponding with those required by silver dibromacetate, viz,, 33·23 p. c., and on examining them they were found to consist of that substance.

Having established this curious fact, it was necessary to find out the nature of the product which accompanied the dibromacetic acid in this decomposition. After making several experiments it was believed to be *glyoxylic acid.*

To determine this, about 18 grams of dibromacetic acid were made into its silver salt, and decomposed by boiling with water, and the resulting acid solution was neutralised with calcium carbonate and filtered. On cooling, the solution was inclined to gelatinise, but on leaving it in a vessel surrounded by hot sand, so as to cause it to cool slowly, it deposited about 3 grams of crystals, and when further concentrated a further small quantity was deposited. These were undoubtedly *calcium glyoxylate.* Nevertheless a calcium determination was made.

·292 of substance gave
·1795 of $CaSO_4$ = 18·07 p. c. calcium.

The formula $C_4H_6Ca''O_8$ requires 18·0 p. c.

The mother-liquors from these crystals contained nothing but calcium dibromacetate.

From these results it is evident that silver dibromacetate when boiled with water yields only dibromacetic and glyoxylic acids, thus—

$$\underset{\text{Silver dibromacetate.}}{2(C_2HBr_2AgO_2)} + 2H_2O = \underset{\text{Dibromacetic acid.}}{C_2H_2Br_2O_2} + \underset{\text{Glyoxylic acid.}}{C_2H_4O_4} + 2AgBr.$$

As this decomposition is remarkable, it was thought desirable to see if the products were really produced in the ratios indicated by the above equation.

For this purpose recourse was had to the well known decomposition of glyoxylic acid into oxalic and glycollic acids when treated with calcium hydrate, it having been found previously from experiment that dibromacetic acid did not yield oxalic acid under these circumstances. The following quantitative experiment was made:—

4·586 grams of silver dibromacetate were boiled until silver bromide ceased to form, and the solution after filtration mixed with an excess of pure calcium hydrate. It was then heated until it boiled, and afterwards acidified with acetic acid. The calcium oxalate which had been produced was collected, washed, ignited, &c. In this manner ·363 gram of calcium carbonate was obtained, equivalent to 7·1 per cent. of oxalic acid from the silver dibromacetate used.

Now as two molecules of glyoxylic acid are required to produce one of oxalic acid, it follows from the above equation that four molecules of silver dibromacetate would be necessary to produce one of oxalic acid. This, if calculated, is found to be in the proportion of 100 parts of silver salt to 6·9 parts of oxalic acid, which closely corresponds with the above experiment, and therefore proves the correctness of the equation.

These experiments show how the mistake occurred in supposing that bromoglycollic acid resulted on boiling silver dibromacetate with water, because a mixture of dibromacetic acid and glyoxylic acid in the proportions produced in this reaction has the composition of that substance.

$$\begin{array}{l} C_2H_2Br_2O_2 \\ C_2H_4\ \ O_4 \end{array}$$

$$C_4H_6Br_2O_6 = \underset{\text{Bromoglycollic acid.}}{2(C_2H_3BrO_3)}$$

It is difficult to understand the manner in which silver dibromacetate yields these products when boiled with water. It may perhaps be that bromoglycollic acid is first formed as the salt is decomposing, and being unstable is immediately acted upon by the undecomposed portions of the silver dibromacetate, thus:—

I. $C_2HBr_2AgO_2 + H_2O = C_2H_3BrO_3 + AgBr.$

II. $C_2H_3BrO_3 + C_2HBr_2AgO_2 + H_2O = C_2H_4O_4 + C_2H_2Br_2O_2 + AgBr.$

Decomposition of Silver Dibromacetate when heated with Alcohol.

Perfectly dry silver dibromacetate when heated to 100° C. with absolute alcohol quickly decomposes with formation of silver bromide. On filtering this off and allowing the alcoholic fluid to evaporate gently, a product is obtained which consists of an ethereal liquid and an acid. The latter was removed from the oily product by means of water, and when converted into a silver salt gave the following numbers:—

·0979 of substance gave
·0574 of AgBr = 33·68 p. c. silver.

showing it to be dibromacetic acid.

The ethereal product was distilled and was found to boil at about 193—195°. It was analysed, but no definite results were obtained. It contained from 32 to 33 p. c. bromine. It is probably a mixture of dibromacetic and diethylglyoxylic ether, for when treated with ammonia it yields dibromacetamide, and on evaporating the mother-liquors from this brilliant plates like diethylglyoxylamide are obtained.

Decomposition of Silver Dibromacetate when heated with Dry Ether.

When heated to 100° C. in a sealed tube with ether the perfectly dry salt decomposes with formation of silver bromide, a small quantity of carbonic acid being also produced. On filtering off the ethereal fluid and evaporating, a thick oily product is left behind. It appears to be impossible to obtain this product in a perfectly pure state, as it cannot be distilled without decomposition. It is generally contaminated with a small quantity of a substance having a very irritating odour; this is removed partially by passing dry air through it whilst heated to 100° C. In order to purify it further it was redissolved in ether and kept over dry sodium carbonate for several hours, filtered, the excess of ether distilled off, and further separated by passing dry air through the oily product whilst heated in the water-bath. On analysis it did not give very satisfactory numbers. The following are the best obtained:—

I. ·2950 of substance gave
·4017 of AgBr.
II. ·3495 of substance gave
·2293 of CO_2 and
·0558 of H_2O.

The formula $C_4H_2Br_2O_4$ requires the following percentages:—

		Calculated.		Found.
C_4	=	48	17·72	17·89
H_2	=	2	·73	1·77
Br_2	=	160	58·39	57·94
O_4	=	64	23·36	—
		274	100·00	

The above formula represents this substance as formed by the decomposition of two molecules of silver dibromacetate with separation of two molecules of silver bromide.

$$2(C_2HBr_2AgO_2) = C_4H_2Br_2O_4 + 2AgBr.$$

This formula is also confirmed by the products of decomposition of this body. If a quantity be mixed with alcohol and a little sulphuric acid, on dilution an oil separates having an irritating odour, which when treated with ammonia gives dibromacetamide, showing it to be dibromacetic ether.

If left in contact with water it gradually dissolves, forming an acid solution. On fractionally precipitating this with silver nitrate the first crop gave the following numbers:—

·2926 of substance gave
·1765 of AgBr = 34·68 p. c. silver,

evidently silver dibromacetate containing a small quantity of glyoxylate.

Another portion was dissolved in water and the solution neutralized with calcium carbonate; after concentration a crop of crystals of calcium glyoxylate separated. A calcium determination of this gave the following results:—

·0424 of substance gave
·0262 of $CaSO_4$ = 18·18 p. c. calcium.

calcium glyoxylate requires 18·01 p. c.

Therefore this oily substance, when decomposed with water, is resolved into dibromacetic and glyoxylic acids, thus:—

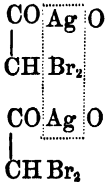
$$C_4H_2Br_2O_4 + 2H_2O = C_2H_2Br_2O_2 + C_2H_4O_4.$$

When distilled it is decomposed, yielding carbonic oxide and dibromacetic acid; a quantity of a gummy product is also formed somewhat like tartaric anhydride.

The first part of this decomposition may be represented thus:—

$$C_4H_2Br_2O_4 = 2CO + C_2H_2Br_2O_2.$$

The formation of this substance from silver dibromacetate is difficult to understand; half only of the dibromacetyl contained in the silver dibromacetate used being decomposed, the rest remaining unchanged; thus:—



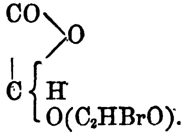
$$\begin{array}{lll} CO & \boxed{\begin{array}{l} Ag \\ \\ Br_2 \\ \\ Ag \end{array}} & \begin{array}{l} O \\ \\ \\ \\ O \end{array} \\ | & & \\ CH & & \\ & & \\ CO & & \\ | & & \\ CH\,Br_2 & & \end{array}$$

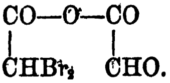
This curious reaction may perhaps be explained if we assume that a bromoglycollide is first formed, and as quickly as it is produced reacts upon the undecomposed silver dibromacetate, thus:—

I. $C_2HBr_2AgO_2 = C_2HBrO_2 + AgBr.$
Silver dibromacetate. Bromoglycollide.

II. $C_2HBrO_2 + C_2HBr_2AgO_2 = C_4H_2Br_2O_4 + AgBr.$
New product.

This new product appears to possess the properties of an anhydride, and may be written either as a dibromacetoglyoxyllide or as a double anhydride, thus:—





$$\begin{array}{ccc} \mathrm{CO} & \text{—O—} & \mathrm{CO} \\ | & & | \\ \mathrm{CHBr_2} & & \mathrm{CHO.} \end{array}$$

Silver dibromacetate undergoes decomposition spontaneously when kept, and the decomposed salt when treated with water yields a solution of dibromacetic and glyoxylic acids.

Glyoxylic Acid.

Being desirous of making a further examination of glyoxylic acid and some of its derivatives, it was necessary to prepare a quantity of this substance, and the following process was employed:—

Forty or fifty grams of silver dibromacetate were boiled with water until decomposed, and the resulting solution of dibromacetic and glyoxylic acids filtered from the bromide of silver formed. Carbonate of silver was then carefully added to the clear solution until it was no longer acted upon, and the resulting mixture of silver salt boiled until silver bromide ceased to be formed. After this latter substance had been separated by means of a filter the acid liquid was concentrated on the water-bath. It usually contained a small quantity of silver in solution, owing to the addition of a slight excess of silver carbonate in the previous operation. This was not found to be injurious, and in fact was useful in removing the last traces of bromine, which it separated as the solution concentrated. When the product was reduced to a somewhat small bulk, hydrochloric acid was carefully added just in sufficient quantity to remove the last traces of silver; and after filtration the solution was further concentrated under a bell jar over sulphuric acid. In the course of a week or so the liquid, which had become syrupy, gradually deposited crystals; these slowly increased in quantity; when a considerable crop had formed, the thick mother-liquor was decanted and the crystals afterwards pressed strongly between bibulous paper, the resulting crystalline cake was then broken up and dried in a vacuum over sulphuric acid. The mother-liquors were again placed under a bell-jar over sulphuric acid, and in the course of a week or so became a nearly solid mass of crystals.

The following combustions were made of the product after drying for fourteen days in a vacuum:—

I. ·29405 of substance gave
·2814 of CO_2 and
·1149 of H_2O.

II. ·2428 of substance gave
·2317 of CO_2 and
·0970 of water.

These numbers show that the crystals were pure glyoxylic acid, having the formula, $C_2H_4O_4$.

	Calculated.		Found.	
			I.	II.
C_2 =	24	26·08	26·09	26·02
H_4 =	4	4·34	4·34	4·43
O_4 =	64	69·58	—	—
	92	— 100·00		

Several preparations were made of this acid, and it was always obtained in the crystalline condition.

Pure glyoxylic acid crystallises apparently in oblique rhombic prisms; it is, however, very difficult to observe the form of the crystals, as they are small and rather confused, and also produced in a very thick fluid, in which it is only possible to view them, because when removed they deliquesce very rapidly. This acid is very soluble in water and alcohol. It tastes very like tartaric acid. When heated it melts to a syrupy liquid; it cannot be distilled without decomposition.

Its aqueous solution if quickly evaporated over sulphuric acid in a vacuum, does not usually crystallise, but becomes a gummy mass; if, however, the vacuum be dispensed with, so that the evaporation takes place slowly, crystals are obtained.

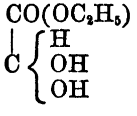
The process for the preparation of this acid is easily understood by the following equations:—

$$2C_2HBr_2AgO_2 + 2H_2O = C_2H_4O_4 + C_2H_2Br_2O_2 + 2AgBr.$$

The resulting mixture of dibromacetic and glyoxylic acids being then converted into silver salts by the silver carbonate, decomposes as follows:—

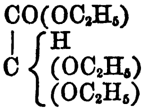
$$C_2H_3AgO_4 + C_2HBr_2AgO_2 + 2H_2O = 2C_2H_4O_4 + 2AgBr.$$

A portion of crystallised glyoxylic acid was heated with absolute alcohol in a sealed tube for five hours, at 120°—130°, in the hope of obtaining the ether—



$$\begin{array}{l} CO(OC_2H_5) \\ | \\ C\left\{\begin{array}{l} H \\ OH \\ OH \end{array}\right. \end{array}$$

The product was a colourless liquid, which gave numbers showing it to have the composition—



$$\begin{array}{l} CO(OC_2H_5) \\ | \\ C\begin{cases} H \\ (OC_2H_5) \\ (OC_2H_5) \end{cases} \end{array}$$

The following are the numbers obtained:—

I. ·1983 of substance gave—
·3900 of CO_2, and
·1625 of H_2O.
II. ·2929 of substance gave—
·5758 of CO_2, and
·2357 of H_2O.

	Calculated.		Found.	
			I.	II.
C_8 =	96	54·54	53·63	53·61
H_{16} =	16	9·09	9·10	8·94
O_4 =	64	36·37	—	—
	176	100·00		

Although these results are not so good as could be desired, they undoubtedly show that the product is diethylglyoxylate of ethyl, any other possible ethylic derivative requiring much lower percentages of carbon. The amount of product at my disposal being small, I was unable to purify it so thoroughly as I could have wished; otherwise I have no doubt better numbers would have been obtained.

Sodium Glyoxylate.—A solution of crystallised glyoxylic acid, when neutralised with sodium carbonate and concentrated, yields a hard crystalline sodium salt. This, when recrystallised and dried at 100° C., gave the following numbers on analysis:—

I. ·3038 of substance gave—
·1928 of Na_2SO_4 = 20·55 p. c. sodium.
II. ·232 of substance gave—
·146 of Na_2SO_4 = 20·38 p. c. sodium.

Theory for $C_2H_3NaO_4$ = 20·17 p. c.

Potassium Glyoxylate.—This salt prepared as the above, but substituting potassium for sodium carbonate, is obtained as an easily soluble crystalline salt. It cannot be dried at 100°, as it swells up and decomposes at that temperature. Dried in a vacuum it gave the following numbers on analysis:—

I. ·2658 of substance gave—
·1776 of K_2SO_4 = 29·95 p. c. potassium.

II. ·2046 of substance gave—
·1375 of K_2SO_4 = 30·12 p. c. potassium.
III. ·236 of substance gave—
·155 of K_2SO_4 = 29·44 p. c. potassium.

Theory for $C_2H_3KO_4$ = 30·0 p. c.

Glyoxylic acid and Ammonia.—The product obtained by Dr. Debus, by the decomposition of calcium glyoxylate with ammonium oxalate, and generally known as ammonium glyoxylate, being the compound that most favours the formula $C_2H_2O_3$ for glyoxylic acid, and C_2HRO_3,H_2O for the glyoxylates, is necessarily of considerable interest; further experiments were therefore made to determine whether or no it be a true salt.

I. A quantity of calcium glyoxylate obtained from the acid produced by oxidizing alcohol with nitric acid, was dissolved in water, and the theoretical quantity of a neutral solution of ammonium oxalate added, both solutions being cold. On filtering off the calcium oxalate, a clear neutral fluid was obtained. This was evaporated over sulphuric acid in a vacuum, but it was observed that it gradually became acid to test-paper, the acidity increasing until crystals separated out. The crystals were washed with cold water, but when dissolved in cold water were still found to be decidedly acid. They were dissolved and recrystallised again by evaporation in a vacuum, but were still acid to test-paper.

II. Another quantity of this product was prepared in the same manner, using calcium glyoxylate prepared from dibromacetic acid, and the solution before evaporation in a vacuum, rendered slightly alkaline with ammonia. The crystalline product was also in this case acid to test-paper.

III. A quantity of a solution of crystallised glyoxylic acid was neutralised slowly with dilute ammonia and evaporated in a vacuum; the solution gradually became acid, and deposited crystals, which were acid to test-paper, even after recrystallisation.

As this derivative of glyoxylic acid dissolves but slowly in cold water, its acidity is most readily seen by placing a little of it in powder, on wet, blue litmus paper. With ammonia it behaves like an acid, inasmuch as it dissolves in it with great facility.

The following analyses were made of different specimens of this substance:—

*I. ·2389 of substance gave—
·2311 of CO_2.

---

* The hydrogen was lost.

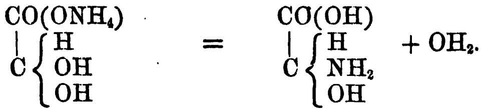
II. ·1480 of substance gave—
·1416 of CO_2, and
·0753 of H_2O.
III. ·2115 of substance gave—
·2020 of CO_2 and
·1082 of H_2O.

	Theory for $C_2H_5NO_3$.	Found.		
		I.	II.	III.
Carbon	26·37	26·38	26·09	26·04
Hydrogen	5·49	—	5·58	5·68

These numbers correspond with those obtained by Dr. Debus, but as they agree almost equally with an acid ammonia salt and also glyoxylic acid, it was thought desirable to determine the nitrogen in this body. Dr. Frankland kindly had a determination made for me by the process he employs for water analysis, and the ratio of carbon to nitrogen was found to be practically as 2 : 1; therefore the above formula is evidently the correct one for this substance.

Seeing that the glyoxylates, as those of potassium and sodium, are neutral to test-paper, and also that the freshly prepared solution of the ammonium salt obtained by double decomposition is also neutral, some change must evidently take place in this salt during its evaporation in a vacuum over sulphuric acid, seeing it becomes acid, without loss of nitrogen. This would indicate that the ammonium left the CO(OH) group for some other. At first sight this may appear strange, but we must remember that Dr. Debus has already shown that neutral glyoxylates will remove ammonia from its salts.

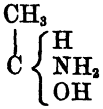
From these considerations I am led to infer that this so-called ammonium glyoxylate is not a true salt, but a product resulting from its decomposition. The change which the ammonium salt, which is undoubtedly at first formed, undergoes, may perhaps be as follows:—



$$\begin{array}{l} CO(ONH_4) \\ \mid \\ C\left\{\begin{array}{l} H \\ OH \\ OH \end{array}\right. \end{array} = \begin{array}{l} CO(OH) \\ \mid \\ C\left\{\begin{array}{l} H \\ NH_2 \\ OH \end{array}\right. \end{array} + OH_2.$$

Ammonium glyoxylate. Amidoglyoxylic acid.

This last compound would be a substance analogous to aldehyde-ammonia in which CH_3 is replaced by CO(OH)—



$$\begin{array}{l} CH_3 \\ \mid \\ C\left\{\begin{array}{l} H \\ NH_2 \\ OH \end{array}\right. \end{array}$$

Aldehyde-ammonia.

A portion of the ammonia derivative of glyoxylic acid was mixed with dilute ammonia, in which it is very readily soluble, far more so than in water. The solution was evaporated in a vacuum. It dried up to a glassy uncrystalline mass, and on analysis gave the following numbers:—

·200 of substance gave
·2040 of CO_2 and
·1147 of H_2O,

showing it to contain 27·81 per cent. of carbon and 6·37 per cent. of hydrogen.

A determination of carbon and nitrogen showed it to contain these elements in the ratio of 4 : 3. The nearest formula corresponding with these numbers is—

$$C_4H_{11}N_3O_5 = C_2H_5NO_3 + C_2H_6N_2O_2$$

or a compound of amido- and diamido-glyoxylic acid; but the substance was of too indefinite a nature to form any decided conclusions from.

The following derivative obtained with aniline and glyoxylic acid favours the view that the ammonia derivative of this acid has the constitution assigned to it, namely, that it is an amido acid. This substance has already been referred to in the paper by Mr. Duppa and myself.

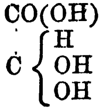
If instead of using ammonium oxalate in the preparation of the so-called ammonium glyoxylate, oxalate of aniline be employed, calcium oxalate separates; and on filtering this off a clear solution is obtained, doubtless glyoxylate of aniline. It, however, quickly changes, becomes yellow, and deposits an orange-coloured powder. This peculiar substance does not possess the properties of a salt, but is both an acid and a base, so that the aniline must have left the COOH group.

This substance is easily soluble in ammonia, and when the solution is evaporated in the water-bath it forms an orange glassy substance which is a soluble ammonia salt. With nitrate of silver a solution of the compound forms an amorphous pale yellow bulky silver salt which can be washed only on a vacuum filter. Several specimens were analysed, but the results were not very concordant, the percentage of silver generally being between 32 and 36 per cent.

It also dissolves in dilute hydrochloric acid, and when evaporated to dryness the solution leaves a soluble hydrochloride containing about 20 per cent. chlorine. This gives with platinum tetrachloride a platinum salt containing about 18 per cent. platinum.

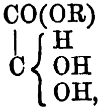
This peculiar aniline derivative does not crystallise; a great many analyses of it have been made, but no satisfactory conclusions as to its formula have as yet been obtained. When distilled with strong potassium hydrate it decomposes and aniline distils over.

From the foregoing results and considerations it appears that undoubtedly the formula of glyoxylic acid is—



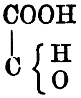
$$\begin{array}{l}CO(OH)\\ \quad|\\ C\left\{\begin{array}{l}H\\ OH\\ OH\end{array}\right.\end{array}$$

and its anhydrous salts—



$$\begin{array}{l}CO(OR)\\ \quad|\\ C\left\{\begin{array}{l}H\\ OH\\ OH,\end{array}\right.\end{array}$$

and, therefore, it contains two hydroxyls in union with one atom of carbon. The substance—



$$\begin{array}{l}COOH\\ \quad|\\ C\left\{\begin{array}{l}H\\ O\end{array}\right.\end{array}$$

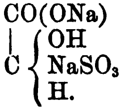
is at present unknown, though its existence is of course probable.

We have the following lists of substances confirming this view:

Glyoxylic acid	$C_2H_4O_4$
Sodium glyoxylate	$C_2H_3NaO_4$
Potassium glyoxylate	$C_2H_3KO_4$
Calcium "	$C_4H_6CaO_8$
Silver "	$C_2H_3AgO_4$
Ethyldiethylglyoxylate	$C_2H(C_2H_5)_3O_4$
Diethylglyoxylamide	$C_2H_3(C_2H_5)_2NO_3$.

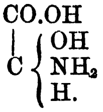
The compound of sodium bisulphite and glyoxylic acid and the ammonia derivative might also be added:

The bisulphite of sodium compound—



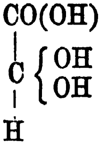
$$\begin{array}{l}CO(ONa)\\ \quad|\\ C\left\{\begin{array}{l}OH\\ NaSO_3\\ H.\end{array}\right.\end{array}$$

Ammonia compound—



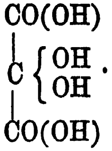
$$\begin{array}{l}CO.OH\\ \quad|\\ C\left\{\begin{array}{l}OH\\ NH_2\\ H.\end{array}\right.\end{array}$$

It is very possible that mesoxalic acid has the formula $C_3H_4O_6$, and not $C_3H_2O_5$; its so-called ammonium salt being possibly a product of decomposition like that of glyoxylic acid. This appears not improbable, as mesoxalic acid may be considered as glyoxylic acid with one atom of hydrogen replaced by CO(OH):



$$\begin{array}{l} CO(OH) \\ | \\ C\begin{cases} OH \\ OH \end{cases} \\ | \\ H \end{array}$$

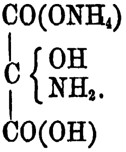
Glyoxylic acid.



$$\begin{array}{l} CO(OH) \\ | \\ C\begin{cases} OH \\ OH \end{cases}. \\ | \\ CO(OH) \end{array}$$

Mesoxalic acid.

The metallic derivatives of this acid and apparently its ether favour this view. The ammonia derivative being the only exception. This may, however, be constituted thus—



$$\begin{array}{l} CO(ONH_4) \\ | \\ C\begin{cases} OH \\ NH_2. \end{cases} \\ | \\ CO(OH) \end{array}$$

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Effect produced by the Admixture of Foreign Substances with Charcoal in the production of Carbon Points for the Electric Light. By M. GAUDUIN (*Compt. rend.*, lxxxiv, 218—219).—The following bodies were introduced into the carbon pencils, to the extent of 5 per cent.:—Calcium phosphate, chloride, borate, and silicate; precipitated silica; magnesia; magnesium borate and phosphate; alumina, and aluminium silicate.

Calcium phosphate was completely decomposed, and the oxide partly reduced; the resulting fumes of phosphoric anhydride and lime rendered the light twice as brilliant as that produced by ordinary gas-carbon poles. Calcium chloride, borate, and silicate were also decomposed and the anhydrides volatilised.

The introduction of silica into the pencils reduced their conductibility and diminished the light produced.

The magnesium salts were decomposed and reduced; the fumes formed by the burning metal and by the phosphoric anhydride increased the intensity of the light, but the augmentation was not so great as with calcium phosphate under similar circumstances.

Alumina and aluminium silicate were decomposed with greater difficulty, and required therefore a stronger current. The aluminium vapour burned with a bluish feebly luminous flame. The flame and smoke which always accompanied these electro-chemical lights appeared so great an obstacle to their use for illuminating purposes that the experiments were discontinued. J. W.

The Electric Conductivity of Acids in Aqueous Solution. By F. KOHLRAUSCH (*Pogg. Ann.*, clix, 233—275).—The acids experimented upon were sulphuric, nitric, hydrochloric, hydrobromic, hydriodic, phosphoric, oxalic, tartaric, and acetic. The numerous series of determinations detailed in the paper have reference to two points chiefly—the relation of the conductivity to the strength of the solution, and the influence of temperature. Some interesting and unlooked for results are recorded, especially as regards *sulphuric acid*. Fused SO_3, on the one hand, and water, on the other, are equally non-conductors of the current. Between these extremes the author has measured the conductivity of solutions containing known percentages of sulphuric acid, and he finds that the curve which expresses the relation of conductivity to percentage of acid in the liquid has at least three maxima and two minima. One of the latter occurs when the solution contains 84·3 per cent. of acid. Now 84·48 per cent. corresponds with the easily crystallised hydrate, $H_2SO_4 + H_2O$. The highest maximum occurs at 30·4 per cent., when the conductivity is

80 times greater than that of H_2SO_4. As to the supersaturation of H_2SO_4 with SO_3, the conductivity increases; one maximum at least must fall between H_2SO_4 and SO_3. At and near the strength 73·18 per cent., corresponding with $H_2SO_4 + 2H_2O$, the curve of conductivity shows, however, no special character. *Phosphoric acid* gives a curve differing from the rest, as it rises to the maximum (about 35 per cent.) in a line almost straight, and falls in a nearly symmetrical manner. For *acetic acid* the maximum is attained when the solution contains 1 part by weight of $C_2H_4O_2$, to 5 parts of water; and then the conductivity is at least 2,000 times better than that of water, and 38,000 times better than that of the concentrated acid.

The maximum conducting powers at 18° of various liquids take the following order, beginning with the highest. Nitric, hydrochloric, and sulphuric acids; potash, ammonium chloride, ammonium nitrate, potassium bromide, potassium chloride, soda, ammonium sulphate, potassium carbonate, sodium chloride. Below these come phosphoric acid and the chlorides of the earth-metals; potassium nitrate, copper chloride, potassium sulphate, oxalic acid, zinc sulphate, copper sulphate, tartaric acid, acetic acid, ammonia.

When the liquid has a minimum of conductivity, an increase of temperature raises the minimum proportionately.

When the percentage content of solutions of nitric, hydrochloric, hydrobromic, or hydriodic acids is multiplied by the specific gravity and divided by the molecular weight, the result represents the number of molecules in equal volumes; and it is very remarkable that when these are equal, in the case of the four acids named above, the conductivities are also equal or nearly so. R. R.

Spectra of Metals at the Base of Flames. By M. GOUY (*Compt. rend.*, lxxxiv, 231—234).—When a mixture of gas and air burns, as in Bunsen's arrangement, the flame has an interior cone for its base, at the surface of which combustion begins. This surface is brilliant, of a blue colour, and like the flame proper gives the carbon spectrum. If, however, the combustible mixture holds in suspension any saline particles, the surface of the cone gives a spectrum which differs materially from that of the flame of which it forms the base. A moderately strong solution of a salt is pulverised by means of a jet of compressed air, and the saline dust introduced into the flame in a suitable manner. Two spectra may then be observed, the one above the other. The rays forming the lower spectrum are all of the same height, and are produced by the light of the blue surface; the upper spectrum is formed by the flame itself, and overlaps the lower spectrum by reason of the peculiar form of the flame.

The spectra of fourteen salts are recorded, of which the details respecting lithium may be taken as an example. The upper spectrum of this salt shows a brilliant red ray and a weaker orange ray; the red appears equally brilliant throughout its length, while the orange ray at the point where it meets the lower spectrum becomes much more distinctly defined. In the lower spectrum a blue line is visible (γ of the electric spectrum), which terminates at the same height as the carbon rays, and is altogether wanting in the upper spectrum.

In this manner it is shown that the base of the flame gives for a short distance a spectrum which resembles the electric spectrum of the same metal.
J. W.

Contributions to the Theory of Luminous Flames. By K. Heumann (*Liebig's Annalen*, clxxxii, 1—29; clxxxiii, 102—141; and clxxxiv, 206—254).—In the first and second sections of this paper the author considers the effect of the withdrawal of heat upon luminous flames; in the third he brings forward experimental proof of the presence of solid carbon particles in the luminous flames of hydrocarbons. He first shows that the burner exercises a cooling action upon the ignited gas issuing from it, and that the point at which the luminosity of the flame begins is therefore situated at some distance from the orifice of the burner. The same reason explains the fact that a candle flame does not actually touch the wick, and also the fact that a flame does not directly come into contact with a solid body held within it. When the combustible gas is mixed with an indifferent gas, or is caused to issue from the burner under high pressure, the cooling action is increased, and the distance between flame and burner is therefore rendered greater. If the velocity of the issuing gas be greater than the velocity of propagation of ignition throughout the gas, no ignition takes place, and it is only when the former velocity has diminished and has become equal to the latter that the flame makes its appearance. If the burner be heated, or if the issuing gas be itself raised in temperature, then the rate of propagation of ignition is increased, and the flame appears at a point nearer to the burner than that at which it had been previously seen. If a metallic wire be held between the flame and burner, and be moved towards the latter, the space intervening between the flame and burner is diminished. This is accounted for by the protecting influence exercised by the advancing wire upon the gaseous particles behind it; these particles are sheltered from the cooling action of the rushing stream of gas, and hence they become ignited.

The author suggests that determinations of the velocities of ignition of various gases should be made, under conditions such that the velocity of propagation of ignition should be equal to the velocity of the stream of gas at the point where the flame begins.

A cold object brought into a luminous flame causes a suspension of the process of combustion in its immediate neighbourhood, and at the same time materially diminishes the luminosity throughout a considerable space around itself. The deposition of soot upon such a cold object is generally supposed to be proof of decreased temperature, but it is shown that a decrease in the temperature of the flame causes a diminution in the quantity of soot deposited. Further it is shown that soot is deposited upon a heated surface held in an ordinary luminous flame; this soot is, however, quickly burned away, inasmuch as it is impossible to altogether prevent admission of air. The surface collecting the soot is compared to a redoubt stopping the progress of the balls fired against it.

The hypothesis which the author puts forward to account for these and other facts is as follows. Carbon containing luminous materials may burn with luminous flames, *i.e.*, with separation of carbon; or without luminous flames, *i.e.*, without separation of carbon, according as a certain temperature, which differs for each material, is or is not maintained. If the combustible material be diluted with indifferent gases, a higher temperature must be maintained in order that a luminous flame shall be produced than if it be not so diluted. A porcelain rod was held in the upper (hot) portion of a luminous flame; soot was deposited. The same rod was brought into the lower (cooler) portion of the same flame; no soot was deposited. In the former case the cooling action of the porcelain was not sufficient to reduce the temperature of the flame below the point at which carbon was separated; in the latter case the temperature was reduced below this point.

The action of burners upon decreasing luminosity of flames is considered. It is shown experimentally that burners constructed of a material having a high conductivity for heat cause a greater diminution in the luminosity of the flame of the gas issuing from them than is caused by burners having a lower conductivity for heat. If the burner be heated the flame becomes more luminous, because the flame is itself enlarged thereby, and carbon is also sooner separated in the flame, and separated at a higher temperature. Any change in the chemical composition of the gas which may be brought about by heating the burner, or by heating the gas itself, is without appreciable effect upon the luminosity.

The author draws a distinction between "light effect" of the whole flame and "intensity of light" of the various constituent parts of the flame. He suggests that in practical photometric observations the total light effect should be determined, and also the maximum quantity of light obtained by allowing the rays to pass through a small and accurately measured opening in a shade placed between the flame and the diaphragm of the photometer. The numbers so obtained might be regarded as approximative values of the relative "intensities of light" of the most brilliant parts of the various flames.

The principal facts adduced in proof of the presence of solid carbon particles in ordinary luminous flames are as follows:—

Chlorine, when admitted into a non-luminous or feebly luminous flame, causes a marked increase in luminosity. But chlorine decomposes hydrocarbons at a red heat with separation of carbon.

A rod held in a luminous flame becomes covered with soot only on that surface against which the issuing gas impinges. Were the deposition of soot occasioned by the cooling action exerted by the rod upon the flame, this deposition would take place equally on all sides of the rod.

Heated surfaces become covered with soot when held in luminous flames. This would not be the case if the deposition of soot were a result of the condensation of heavy vapours.

If two flames be caused to impinge upon each other with a proper velocity and at a proper angle, or if a flame be caused to play against the convex side of a platinum basin placed vertically, the concave side being strongly heated, the solid carbon particles in the flame gather themselves together into larger masses, and the flame becomes filled with glowing points. The soot deposited from such a flame is very coarse-grained.

The luminous portion of an ordinary flame is not more transparent than the layer of smoke which rises from burning turpentine, and which certainly contains solid matter.

The flame of hydrogen rendered luminous by the presence of solid chromic oxide is as transparent as an ordinary hydrocarbon flame.

Those flames which undoubtedly owe their luminosity to the presence of solid matter, throw characteristic shadows when viewed in sunlight against a white screen. Luminous flames free from solid matter cast no shadows. Ordinary luminous hydrocarbon flames cast distinct shadows, therefore these flames contain solid matter.

If the soot which is deposited upon a cold body held in a luminous flame existed in that flame in the form of vapour, it would be possible again to vaporise it by applying heat. Stein has shown that this cannot be done.

Stein has also shown that the soot which is deposited from ordinary luminous flames does not contain more than 0·9 per cent. of hydrogen.

M. M. P. M.

On a Remarkable Regularity in the Volume-Relations of Definite Series of Compounds. By H. Schröder (*Deut. Chem. Ges. Ber.*, ix, 1888—1893).—When an element like silver and a series of its compounds, or a component like magnesia and a series of its compounds, have volumes which stand exactly in simple relations to each other, the author expresses the fact by saying that they have equal volume-masses or equal steres. Their volumes may be represented in fact as multiples in whole numbers of a common volume-mass or common stere.

There is, as a rule, one of the elements of a compound which impresses its own volume-mass or stere on the whole compound, and makes itself the prevailing determining, or controlling element in a whole series of otherwise very different compounds; and thus it would seem as if one constituent of a compound exerted a dominating or assimilating influence on the volume of all the remaining constituents. The author's investigations show that in silver oxide, carbonate, acetate, benzoate, chloride, iodide, sulphide, telluride, in miargyrite and red silver ore, the volume mass or stere of the silver dominates. In corundum, beryl, and andalusite the aluminium stere prevails, and this is identical with the stere of silver, gold, tellurium, and graphite. In quartz and cyanite (disthene) the stere of silicon prevails. In periclase, chrysolite, augite, and magnesite, the volume-mass of magnesium dominates. It is identical with the stere of zinc, manganous oxide, calcite, and several other compounds of the magnesium series. The isomerism of andalusite and cyanite is referred to the fact that in andalusite, aluminium, in cyanite silicon is the determining element, while the other constituents are assimilating. G. T. A.

Determination of the Specific Gravities of Fats at High Temperatures. By G. W. Wigner (*Analyst*, 1876, 145).—The method consists in noting the temperature at which glass bubbles sink in melted fats. The bubbles are previously tested in liquids of known gravity. For the details of procedure the original paper must be consulted. M. M. P. M.

Inorganic Chemistry.

Experiments on the Displacement of Chlorine by Bromine from its Compounds with the Elements of the 1st, 2nd, 3rd, 4th, and 8th Groups of Mendelejeff's Natural System. By A. Potilizin (*Chem. Centr.*, 1876, 577—578).—The operation was conducted in sealed glass tubes, from which air had been expelled, at a temperature approaching the melting point of zinc. From the experiments, it was found that the amount of chlorine replaced by bromine, the two being present in molecular proportion, is directly proportionate to the atomic weight of the elements, provided they belong to the same group. The following table shows the relation of the metals:—

	$NaCl$.	KCl.	$AgCl$.		
Group 1	7·16	12·54	33·34		
	$CuCl_2$.	$SrCl_2$.	$BaCl_2$.	$HgCl_2$.	$PbCl_2$.
,, 2	3·2	6·64	9·86	15·16	15·64

These numbers represent the percentage of chlorine replaced by bromine, and are proportional to the atomic weights of the metals. They are independent of the time of action, beyond certain limits. If the number of one of the series is known, the rest may be calculated, and this gives a test of the quantivalence of the metal. Thus Ca = 20 gives a calculated number 6·21, which is nearly twice as great as its experimental value, viz., 3·2. The quantivalence of calcium is therefore seen to be 2. Thus also the atomicity of bismuth, tin, and iron may be found in the following manner:—

	Bi'''.	Sn^{iv}.	Fe_2^{vi}.
Calculated percentage	20·5	8·74	5·87
Quotients	3·35	4·6	5·87

The lower line of numbers approximately represents the quantivalence of the metals. The author proposes to extend his researches, and to determine in this manner the quantivalence of elements of the cerium group. W. R.

Preparation of Hydriodic Acid. By H. Kolbe (*J. pr. Chem.* [3], xv, 172).—The best method of preparing this acid is to add gradually 1 part of ordinary phosphorus to 10 parts of iodine, in a retort filled with carbonic anhydride, heat the resulting fluid mixture of PI_2 and PI_3 for a short time, then drench it, after cooling, with 4 parts of water, and distil. The hydriodic acid thus obtained is quite colourless, and contains no free iodine.

Some manuals (*e.g.*, *Gmelin-Kraut's Handbuch*, i, 366) recommend the use of much larger proportions of iodine and water, the directions being to add gradually 20 parts iodine to 1 part amorphous phosphorus, in 15 parts water, moderate the reaction by cooling, and then distil. The hydriodic acid thus obtained is, however, very weak, and contains a large quantity of free iodine. E. W. P.

On Iodine Chloride. By W. BORNEMANN (*Deut. Chem. Ges. Ber.*, x, 121).—Pure iodine chloride, ICl, is decomposed by water, iodine being set free, and hydrochloric and iodic acids formed; a little iodine chlorine remains, however, in solution. Iodine chloride dissolves in dilute hydrochloric acid, without separation of iodine, and it is even possible to redissolve, by addition of hydrochloric acid, the iodine set free on adding iodine chloride to water, this result being due to the action of hydrochloric on iodic acid.

When chlorine is passed into water containing known quantities of iodine till the whole of the iodine disappears, a separation of iodic acid takes place in concentrated solutions only. In solutions containing less than 1 part of iodine to 1 part of water, no such separation occurs. The whole of the iodine is converted into iodic acid only in solutions containing at least 10 parts of water to 1 part of iodine. When chlorine is passed into concentrated solutions so long as it is absorbed, iodic acid and iodine trichloride are deposited, and the supernatant red-brown liquid gives off iodine trichloride in a vacuum. J. R.

Action of Water on the Chlorides of Iodine. By P. SCHÜTZENBERGER (*Compt. rend.*, lxxxiv, 389—391).—The compounds ICl and ICl_3 are both decomposed by water, the products being iodic acid, hydrochloric acid, and a volatile yellow substance, having a powerful odour, and removable from the aqueous solution by agitation with ether. In the case of the monochloride there occurs also an abundant deposit of iodine. The author's observations lead him to the conclusion that the yellow substance is a compound of monochloride of iodine and hydrochloric acid (ICl.ClH). In the reaction of water on ICl, the quantity of the chloride decomposed is just so much as will furnish sufficient hydrochloric acid to combine with the remainder of the chloride to produce the compound, ICl.ClH. Trichloride of iodine may be regarded as formed of ICl_5 + ICl, and as the former yields with water only iodic and hydrochloric acids, the trichloride should furnish half its iodine to form iodic acid, and the other half to produce the compound, ICl.ClH, a result which the author has experimentally verified. R. R.

Production of Sulphuric Acid in the Combustion of Coal Gas. By W. C. YOUNG (*Analyst*, p. 143).—The gas-referee's apparatus was employed. By a slight modification in the apparatus the author has been able to show that sulphuric acid is practically the sole product of the oxidation of the sulphur in coal gas. M. M. P. M.

Action of Dry Hydrogen Chloride on Sulphates. By C. HENSGEN (*Deut. Chem. Ger. Ber.*, x, 259—261).—Anhydrous magnesium sulphate ($MgSO_4$) is decomposed by dry hydrogen chloride only at the temperature of incipient redness, thus behaving like the sulphates of alkalis and alkaline earths. The hydrated sulphate ($MgSO_4 + 7H_2O$) is decomposed at the ordinary temperature. The crystals melt to a clear liquid, which, after a time, on further absorption of hydrogen chloride, deposits a crystalline powder, converting the whole into a magma.

Anhydrous magnesium sulphate is nearly insoluble in concentrated hydrochloric acid, and the hydrated salt dissolves therein only because its water of crystallisation dilutes the acid. Hence it appears that, in the action of hydrogen chloride on the hydrated salt, the gas is at first absorbed by the water of crystallisation, forming a liquid in which the anhydrous salt is soluble, but as the hydrochloric acid thus formed becomes more concentrated the anhydrous sulphate is gradually deposited. J. R.

Amido-sulphonic Acid. By EMIL BERGLUND (*Deut. Chem. Ges. Ber.*, ix, 1896—1897).—Ammonium or barium imido-sulphonate (see this Journal, 1876, ii, 44) was dissolved in water and heated to strongly acid reaction. The liquid was then mixed with excess of barium hydrate and boiled till all the ammonia was expelled. After filtration the excess of barium was precipitated with carbonic acid. The barium amido-sulphonate was deposited on standing in long, slender, silky needles.

The formula of this salt is $BaNH_2SO_3$. It is anhydrous and so stable that it may be boiled with hydrochloric acid without change, and is not decomposed when heated alone up to 200°. The author has hopes of being able to prepare this salt from ammonium sulphate. G. T. A.

Behaviour of the Sulphides of the Alkali-metals to Water. by PETER CLAESSON (*J. Prakt. Chem.* [2], xv, 218—221).—Both Kolbe and Thomsen believe that an alkaline sulphide, when dissolved in water, decomposes to form a hydroxide and a hydrosulphide. Kolbe supports this view by the fact that in distilling sodium ethylsulphate with sodium hydrosulphide, prepared by the wet method, the amount of ethyl disulphide is greater the less water was used in the preparation of the hydrosulphide. He supports the ordinary view, that on mixing concentrated solutions of potassium hydroxide and hydrosulphide potassium monosulphide is formed. This view, of course, depends for its accuracy on the equation $Na_2S + 2C_2H_5NaSO_4 = (C_2H_5)_2S + 2Na_2SO_4$. Now sodium hydroxide absorbs mercaptan as easily as it does sulphuretted hydrogen, and this solution behaves like sodium mercaptide. The amount formed depends on the concentration of the solution. Supposing the sodium sulphide to be a mixture of hydroxide and hydrosulphide, mercaptan is first formed by the action of an ethyl sulphate; this mercaptan partially distils over and partly reacts with the caustic soda to form mercaptide. The mercaptide, however, reacts on the ethyl sulphate to form ethyl disulphide. The three equations are these—

(1.) $KSH + C_2H_5.KSO_4 = C_2H_5SH + K_2SO_4$.
(2.) $C_2H_5.SH + KOH = KSC_2H_5 + H_2O$.
(3.) $KSC_2H_5 + C_2H_5KSO_4 = (C_2H_5)_2S + K_2SO_4$.

This series of reactions agrees also with the fact remarked by Kolbe, that less ethyl sulphide is formed the more water is present, for, in that case, less sodium mercaptide is formed. This appears to prove that an alkaline sulphide in aqueous solution is a mixture of a hydroxide and a hydrosulphide. If sulphuretted hydrogen be passed into the retort during the distillation the amount of ethyl sulphide is reduced from 20 to 4 per cent., owing to conversion of the hydroxide into hydrosulphide. W. R.

Action of Dioxide Manganese on Ammonium Nitrate. By J. W. Gatehouse (*Chem. News*, xxxv, 118).—On heating manganese dioxide with ammonium nitrate, a violent action occurs, and if the external temperature is maintained, the action may become so intense as to raise the contents of the vessel to dull redness, when abundance of the red vapours of nitrogen tetroxide are formed. The action begins at 360° F., the point at which nitrate of ammonium itself is decomposed, and if the temperature is kept between 360° and 390°, great frothing occurs and a constant stream of an invisible gas is evolved. This gas is pure nitrogen and is disengaged according to the following equation:—

$$MnO_2 + 4(NH_4.NO_3) = Mn(NO_3)_2 + 8H_2O + 6N.$$

When the temperature is allowed to rise above 400° a more complex action ensues, the manganous nitrate being apparently decomposed into MnO_2, NO_2, and O. An analysis of the gas evolved proved that at temperatures between 360° and 420° F. a mixture of equal weights of manganese dioxide and ammonium nitrate yields pure nitrogen gas, while at a temperature above 420°, nitrogen, dioxide, and oxygen are also evolved from the decomposition of the manganous nitrate first formed. D. B.

Octohedral Borax. By A. Arzruni (*N. Rep. Pharm.*, xxv, 622).—A concentrated solution of common borax maintained at 70° deposits crystals having the composition $Na_2B_4O_7.5H_2O$. These crystals are generally stated to be regular octohedrons. The author finds that they are really hexagonal rhombohedrons. The proportions of the axes are $a : c :: 1 : 1{\cdot}87$. M. M. P. M.

Solubility of Gypsum in Water and in Saline Solutions. By J. Haver Droeze (*Deut. Chem. Ges. Ber.*, x, 330—343).—The author describes the methods by which he has determined the solubilities of gypsum. His results show that 412 parts of pure water at 5·5° C. are required for the solution of 1 part of gypsum, and that the solubility increases with the temperature. For example, 357·9 parts of water at 36° suffice for the solution of 1 part of gypsum.

The presence of chlorides and nitrates of the alkalis and of magnesium increases the solubility of gypsum, saturated solutions of these salts dissolving more than dilute solutions, and nitrates more than chlorides. A $\frac{1}{4 \cdot 8}$ saturated solution of ammonium chloride, however, dissolves more than a saturated solution. Saturated solutions of the corresponding sulphates have different effects: that of potassium sulphate dissolves less gypsum than water; that of sodium sulphate has the same effect as water, that of ammonium sulphate but little more than water, that of magnesium sulphate dissolves no gypsum at all at 14·5° C. R. R.

Purification of Zinc Sulphate. By FR. STOLBA (*Chem. Centr.*, 1876, 700).—The zinc sulphate is purified from manganese and iron by oxidising the latter metals with zinc permanganate prepared from potassium permanganate and zinc silicofluoride. The permanganate is added till the liquid is slightly coloured, and the excess is destroyed by boiling. The liquid is filtered and evaporated, when the sulphate crystallises out in a pure state. W. R.

Zinc Phosphide (Zincum phosphoratum). By H. HAYER (*Chem. Centr.*, 1876, 585—586).—The old method of preparation was by adding pieces of dry phosphorus to zinc melted in a flask. A more recent recipe is to pass phosphorus vapour over melted zinc. Its specific gravity is 4·72; it is volatile, and melts at a higher temperature than zinc. It is stable, except when heated; it then burns to zinc phosphate. It contains 25 p. c. of phosphorus. W. R.

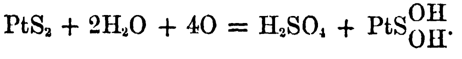
Formation of "Moss Copper." By W. M. HUTCHINGS (*Chem. News*, xxxv, 117).—About ¼lb. of regulus (containing 65·9 per cent. of copper) was fused with borax in a clay crucible, and the molten mass poured into an iron mould. After cooling very slowly the regulus was found to contain a large amount of disseminated copper, the fractured surface showing numerous veins and small nests of needles and jagged points in small cavities in the regulus, even to the naked eye, while a microscope showed the entire surface to be dotted with copper particles. When the copper mass was cooled quickly, very little copper was visible under the microscope. A large button of regulus which had cooled in the mould for some time, so that it had been quite solidified for some minutes, was laid on an anvil and broken in two by a blow with a hammer. It was still too hot to hold in the hand, but had cooled far below redness, even in the centre. At the moment of fracture, the surfaces exposed were clean and lustrous, and showed only little veins and nests and imbedded particles of the disseminated copper when looked at quickly with a lens; but in the course of a minute or two they were seen to become slowly covered with a growth of minute copper filaments, which increased, till in some places it resembled a coarse velvet. After three or four minutes one of the halves was again broken in two, and again the fresh and lustrous surface of regulus exposed, which contrasted strongly with the surface already covered with "moss." In all cases the growth is most extensive on the hotter parts of the surface. The formation of moss copper is similar to that of moss gold and silver, as described by Liversidge, the most curious and interesting fact being the very low temperature at which the moss is formed. When fractured the second time, the pieces had a temperature of not more than 100°. D. B.

Constitution and Properties of "Oxidised Platinum Sulphide." By Ernst von Meyer (*J. pr. Chem.* [2], xvi, 1—22).—Platinum sulphide, PtS_2, which had been prepared by treating a hot solution of $PtCl_4.2KCl$ with hydrogen sulphide, thoroughly washing the precipitate, and drying it on a water-bath, was exposed for several days to the action of the air.

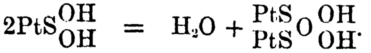
The substance obtained in this manner contains, not only platinum, sulphur, and oxygen, but also chemically combined water. The determination of the platinum was made by strongly heating the substance in a crucible and weighing the residual metal; that of the sulphur, either by oxidation with aqua regia or by treating with hydrogen and finding the amount of hydrogen sulphide evolved; in the latter case the body must be strongly heated, as at low temperatures water alone is formed. The amounts of oxygen and water were determined by means of a current of hydrogen perfectly free from oxygen, the water due to the combination of the hydrogen with the oxygen of the oxidised platinum sulphide plus that which existed in the body being weighed. If carbon monoxide be employed instead of hydrogen, it unites with the oxygen to form carbon dioxide; the amount of oxygen may therefore be obtained distinct from that of the water.

Numerous analyses, some of which are given in detail, were carried out according to the above methods; they show that oxidised platinum sulphide is a hydrate of the body (PtS)O, which itself appears to be incapable of separate existence. In some cases the hydrate PtS^{HO}_{OH} is formed, in others $\begin{matrix}PtS\\PtS\end{matrix}O\begin{matrix}OH\\OH\end{matrix}$. The existence of the latter body only is a matter of absolute certainty.

The formation of these substances is explained by the following equations:—

I. 

$$PtS_2 + 2H_2O + 4O = H_2SO_4 + PtS^{OH}_{OH}.$$

II. 

$$2PtS^{OH}_{OH} = H_2O + \begin{matrix}PtS\\PtS\end{matrix}O\begin{matrix}OH\\OH\end{matrix}.$$

Evolution of a certain amount of sulphurous acid, however, always accompanies the reaction. When platinum sulphide is oxidised by means of chlorine-water, or of a solution of iodine in potassium iodide, the product gives the above reactions with hydrogen and carbon monoxide, but a pure compound is unattainable. The facility with which oxygen replaces one of the atoms of sulphur in platinum sulphide shows that the two sulphur-atoms have different functions; in the oxysulphide the still slighter attachment of the oxygen atom is the cause of the striking oxidising properties of its hydrates.

Hydrogen sulphide is oxidised by these bodies, water being formed, sulphur precipitated, and much heat evolved; sulphurous acid in contact with them is converted into sulphuric acid; hydrogen chloride is but little attacked in the cold, but on heating water is formed, and the free chlorine oxidises the sulphur, producing sulphuric acid. Nitrous and nitric oxides are unaltered; ammonia is rapidly absorbed, a great amount of heat being developed; there is no residue of nitrogen. Oxalic acid, ferrous salts, alcohol, and toluene also undergo oxidation. Liquids and gases dissolved in liquids are acted upon with far less activity than free gases. Oxidised platinum sulphide reduces permanganate of potash, and is also oxidised when heated with free oxygen. F. D. B.

Platonitrites. By L. NILSON (*Bull. Soc. Chim.* [2], xxvii, 242—247).—The author has succeeded in preparing platonitrites of nearly all the metals. The salts are obtained by double decomposition, and, as a rule, they crystallise very well. The platonitrites of glucinum, aluminium, chromium, iron, and iridium furnish, by the evaporation of their solutions, a series of salts of a fine red colour, which the author names *diplatonitrites.* H. H. B. S.

Mineralogical Chemistry.

Symmetrical Growth of Circular Polarising Crystals. By P. GROTH (*Jahrb. f. Min.*, 1876, 663—664).—Two distinct classes of regular growth must be noted, viz., (1) where the growth is simply that of ordinary quartz twins, the +R of one individual being parallel with the −R of the other individual. (2.) Symmetrical twins, one individual being the reflex of the other in relation to a certain face. The latter class is principally confined to crystals exhibiting circular polarization, because the reflex of a dextrorotatory enantiomorphous crystal is always an inversely formed levorotatory crystal. Crystals exhibiting circular polarization do not possess planes of symmetry, therefore any face may be a twin-plane. The scalenohedral quartz crystals from Brazil, described by the author, may be mentioned as examples of this class of crystals, the twin-plane being a face of $\infty P2$, and the trapezohedral quartz crystals from Schneeberg, the twin-plane being also a face of $\infty P2$; but a new twin formation is also observed on crystals from this locality, two twins being united symmetrically parallel to a face of ∞R. The two twins are so united that only the outermost half of each is developed, the twin-plane thus serving at the same time as "contact-plane." Re-entering angles are observed on these twins, but this would not be the case were +R and —R in equilibrium. Optical examination confirmed the crystallographic examination, as a section made parallel to 0P exhibited alternate layers of dextro- and levorotatory substance in each half (I, II, and III, IV), in polarized light also the characteristic black cross of amethyst, and also "Airy's spirals." The author concludes from his observations that a simple twin of dextro- and levo-rotatory quartz was first formed, according to the new law (twin-plane a face of ∞ R), but on the crystal growth continuing, the outer portions of the same were covered with twin-lamellæ according to the other law, thus forming a crystal containing four individuals. (Vierling.)

C. A. B.

Etched Figures on Adular, Albite, Fluorspar, and Sodium Chlorate. By H. BAUMHAUER (*Jahrb. f. Min.*, 1876, 602—607).—Cleavage-pieces of adular parallel to 0P from St. Gotthard were submitted to the etching effect of hydrofluoric acid gas for a few moments. The result of this treatment was the formation of depressions possessing exactly the symmetry of the monoclinic system, and enclosed by six faces, with a seventh corresponding with the basal terminal plane. The six faces belong apparently to three pairs of crystals of the augitic type; the lines or outer edges of the depressions intersecting in the plane, 0P, in one pair (the foremost one) at an angle of about 113°, and in another pair at an angle of 133°. These depressions appear, therefore, to exhibit the form, 0P. ∞ P. $+ m$P (m being unknown), a hemipyramid $+m$Ᵽn, and one having the formula—mⱣ$\frac{3}{2}$, the lines of this form in the plane of 0P intersecting at an angle of 132° 35′, but the value of m is unknown. No etchings were obtained from the faces of ∞ P. Crystals of albite from Zoptau and cleavage-pieces of the same mineral from St. Gotthard were submitted to the etching process, the plane 0P. alone being affected. The depressions thus obtained were pentagonal and undoubtedly triclinic in character, as the author was able to determine the presence of the following forms, viz.:—m_1P . mP . m'P . $m'\bar{\text{P}}'$ ∞ and $m\breve{\text{P}}'$ ∞. These depressions often vary in form and are occasionally distorted.

Wyrouboff described (*Bull. Soc. Chim. de Paris*, 2 série XII, 220) the occurrence of very small octohedrons on the faces of fluorspar crystals, after etching them with sulphuric acid. The author observes the same thing on etched fluorspar crystals, the depressions being square and of small size, and their lateral edges parallel with the combination-edges of ∞ 0 ∞ and 0. Whether they are octohedral or trapezohedral is still uncertain. Large crystals of sodium chlorate (which exhibits circular polarization) were prepared, the salt crystallising in the regular system with a tetratohedral "habit." The negative tetrahedron was the predominating form, the cube and rhombic dodecahedron being quite secondary and also the positive tetrahedron. On slightly etching respectively a dextro- and levo-rotatory negative tetrahedron with water, triangular depressions were obtained, the sides of these depressions being parallel to the combination-edges of the tetrahedron with the right and left-handed pentagon-dodecahedron, from which it may be safely inferred that the depressions are really caused by this form. The difference in position of the depressions is a convenient means of ascertaining whether the sodium-chlorate crystal under examination is a dextro- or levo-rotatory one. No distinct etched figures were obtained upon the positive tetrahedron $+ \frac{0}{2}$, nor upon the faces of ∞ 0. The author concludes from his results that the tetrahedrons observed on sodium-chlorate crystals are not hemihedral, but tetratohedral. C. A. B.

The Isomorphism and Chemical Constitution of Lievrite, Humite, and Chondrodite. By WEBSKY (*Jahrb. f. Min.*, 1876, 660—661).—The analysis of Elba lievrite by Sipöcz and Städeler led to the empirical formula $H_2Ca_2Fe_4Si_4O_{18}$, which constitutes a combination of one molecule of a unisilicate with one molecule of a subsilicate. Humite and chondrodite can also be considered to have a similar constitution. A morphological isomorphism can easily be shown between lievrite and humite, 9 out of the 19 forms observed on lievrite by Descloiseaux possessing nearly the same angles as those observed on 9 faces of humite crystals of the first type. The axial ratio of lievrite is $a : b : c = 1·505382 : 2·258757 : 1$; and in order to bring the forms of lievrite into the same position which vom Rath assigns to humite, we must imagine the brachyaxis of lievrite to be the vertical axis, the macroaxis to be the brachyaxis, and the vertical axis to be the macroaxis, when the following axial ratio is obtained:— $a : b : c = 1·13198 : 1 : 4·516147 = 0·25007 : 0·22142 : 1$. The axial ratio for humite crystals of the first type is $a : b : c : = 1·08028 : 1 : 4·40132 = 0·25719 : 0·227205 : 1·$ according to vom Rath. It is difficult to see an analogy between chondrodite and humite on looking at the results of analyses of these minerals. In order to do so, it must be assumed hypothetically that under certain circumstances, and particularly in the presence of fluorine, the element magnesium plays the part of a hexatomic double-atom forming then a group $Mg_3O_3Fl_2$ or $Mg_3O_2Fl_4$. Chrondrodite from North America and Pargas had apparently the constitution $\left\{\begin{matrix} 5MgSiO_4 \\ Mg_3O_2Fl_4 \end{matrix}\right\}$, $\frac{1}{10}$ to $\frac{1}{3}$ of the magnesium in the lower formula being replaced by iron. Analyses of humite from Vesuvius and Nya Kopparberg give the general formula $\left\{\begin{matrix} m\,Mg_2SiO_4 \\ Mg_3O_3Fl_2 \end{matrix}\right\}$ the value of m oscillating between 5 and 10, a part of the magnesium in the lower formula being replaced by iron, or (in the humite from Nya Kopparberg) by aluminium. The author concludes from the analysis of humite of various types and of chondrodite, that the latter is a different mineral formation from the former. C. A. B.

Notes on Turnerite. By C. O. TRECHMANN (*Jahrb. f. Min.*, 1876, 593—601).—The author examined some fine crystals of this mineral from the Lercholting Alp in the Binnenthal, and submitted them to very accurate measurement with turnerite crystals from Tavetschthal. G. vom Rath (*Sitzb. d. k. bayer, Akad. d. Wissensch.* Nov. 5th, 1870) described the Tavetschthal crystals fully, giving also his measurements by which he concluded that monazite and turnerite are identical. The author's investigations confirm this conclusion in the most unmistakable manner. On Binnenthal turnerite the form — ⅗ ₽ ∞ was observed, which is new to this mineral, but the forms ∞ ₽2 . ½ ₽ ∞ . 2₽2 were absent, also on the turnerite from the Tavetschthal. The forms ∞ ₽3 . — ⅗ ₽ ∞ and ½ ₽ $\bar{\infty}$ have not yet been observed on monazite. The axial relation of turnerite is, $a : b : c : = 0·958444 : 1 : 0·921696$ $\beta = 77° 18'$. Turnerite occurs sometimes accompanied by zenotime, the crystals of the former having a length of from ½ to mm., but some, exhibiting an orthodiagonal development, have occasionally a length of 4 mm. The faces are not so distinct on the Binnenthal turnerite as on the Tavetschthal crystals, there being often a striation or convexity which interferes with the taking of accurate measurements, $\infty P \bar{\infty}$ is always vertically striated; sometimes also the other prismatic faces. The faces + Ᵽ∞ − Ᵽ ∞ − $\frac{3}{5}$Ᵽ∞ are only true on the smallest crystals; on the larger crystals they are convex and drusy. Binnenthal crystals of turnerite are not so pellucid as those from Tavetschthal; their colour is a very striking dark-orange; whilst the colour from the latter locality is yellow or yellowish-brown. Perfect cleavage parallel to the clinopinacoïd. Binnenthal crystals exhibit the following combinations:—

(1.) Thick tabular, ∞ Ᵽ ∞ and + Ᵽ ∞ predominating, pyramids being absent; the commonest form being ∞ Ᵽ ∞ . + Ᵽ∞ . ∞ Ᵽ 2 . ∞ Ᵽ ∞ . ∞ Ᵽ 3 . 2 Ᵽ ∞ . Ᵽ ∞ .

(2.) Short prismatic, ∞ Ᵽ ∞ . 2 Ᵽ ∞ and Ᵽ ∞ predominating. Form ∞ Ᵽ ∞ . 2 Ᵽ ∞ . ∞ Ᵽ ∞ + P . ∞ Ᵽ 2 . + Ᵽ ∞ . ∞ Ᵽ 3 . ∞ Ᵽ ∞ .

(3). Exhibiting macrodiagonal development, characterized by the occurrence of − Ᵽ ∞ and − $\frac{3}{5}$ Ᵽ ∞, which have been observed only on crystals of this type. Form ∞ Ᵽ ∞ . + Ᵽ ∞ . − Ᵽ ∞ . − $\frac{3}{5}$ Ᵽ ∞ . ∞ Ᵽ 2 . ∞ Ᵽ ∞ . ∞ Ᵽ 3 . 2 Ᵽ ∞ . Ᵽ ∞ . + P.

The "habit" of the crystals from Tavetschthal is slightly different from that of the Binnenthal crystals, ∞ Ᵽ ∞ and + Ᵽ ∞ predominating, whilst ∞ Ᵽ ∞ is very small. Nearly all of them exhibit the following combination: ∞ Ᵽ ∞ . + Ᵽ ∞ . ∞ P . ∞ Ᵽ 2 . P 2 Ᵽ ∞ . P ∞ . ∞ Ᵽ ∞ . + P . ′+ 2 Ᵽ 2 . ′+ 3 Ᵽ 3 − P. The form − Ᵽ ∞ is entirely absent. It will be readily observed that the Binnenthal crystals are remarkable for an almost entire absence of pyramids, whilst the Tavetschthal crystals are remarkable for their numerous pyramids. The prism ∞P 3 is peculiar to the former locality, ∞P is peculiar to the latter, and the prism ∞ P 2 is common to both. An examination of the optical properties of turnerite from Tavetschthal was made (the Binnenthal crystals not being sufficiently transparent), when it was observed that the first bisectrix (Hauptschwingungsrichtung) was in the obtuser angle of the crystallographical axes *a* and *c*, forming an angle of 1° 4′ with the vertical axis. The plane of the optical axis is perpendicular to ∞ Ᵽ ∞, the first bisectrix being in the clinodiagonal "principal section," and the second in the orthodiagonal section. Examined in oil, no appreciable horizontal dispersion was observed about the first bisectrix. The crystals exhibited positive double refraction. The other optical properties completely proved the identity of monazite with turnerite. Tavetschthal turnerite was found to be pleochromatic in the direction of the pinacoïds ∞ Ᵽ ∞ and ∞ Ᵽ ∞; the colour in the first direction being brownish-yellow, and in the second leather-yellow. Owing to the paucity of material, the author was unable to determine the specific gravity, or to make a quantitative analysis of the mineral, but a qualitative blowpipe analysis proved the absence of phosphoric acid and the probable presence of cerium oxide. The author gives a table of his measurements of the crystals from both the above-named localities, in conjunction with G. vom Rath; also some excellent drawings of the same. C. A. B.

Idocrase near Drammen. By W. C. Brögger (*Jahrb. f. Min.*, 1876, 661—662).—Occurs between Drammen and Konerud, in Norway, in a very decomposed sedimentary rock, crystallised and crystalline. The rock is penetrated by numerous hollow spaces formed by the weathering of corals, and the idocrase crystals clothe these hollows, particularly those formed by cyathophyllii. These crystals are occasionally 1 c.m. in height; are always attached and exhibit the combination ∞ P . P . ∞ P ∞ . 3P . 3P3 . P∞ . OP. Smaller hollows, such as those formed by halysites, are filled with crystalline granular olivine and grass-green idocrase. Hyacinth-red garnets accompany the idocrase.

Chiastolite-slate, near Eckern.—Found in a black aluminous slate, in shining, sharply-defined prisms $\frac{1}{2}$ to $\frac{3}{4}$ mm. in thickness, and 1 cm. in length. The prisms exhibited the characteristic black kernel and traces of a cross. Most of the crystals were developed parallel to the plane of stratification. C. A. B.

Pachnolite and Thomsenolite. By G. König (*Jahrb. f. Min.*, 1876, 662—663).—The quadratic pachnolite of Hagemann and the separate species of Knop (also called pachnolite) occur together in Greenland. The author obtained a large quantity of material to work upon, and eventually arrived at the following conclusions:—(1.) The mineral analysed by him is identical in constitution with Knop's pachnolite. (2.) It is also identical in form and physical properties with Dana's thomsenolite. (3.) The measurements made were so inaccurate, that the true form of the crystals could not be ascertained. (4.) The mineral examined crystallographically by Knop and Descloiseaux was probably never analysed, as Knop never gave any further particulars concerning it. (5.) The name "pachnolite," being the oldest and most appropriate, should be retained. C. A. B.

Gastaldite (a new Mineral). By J. Strüver (*Jahrb. f. Min.*, 1876, 664—665).—Crystallises in the monoclinic system. Type prismatic, through ∞ P and ∞ Ꝑ ∞, the terminal faces being indistinct. It occurs also pulverulent and fibrous. Prismatic cleavage with an angle of 124° 25′. Conchoïdal fracture H. 6—7, sp. gr. 3·044. Colour blackish-blue to sky-blue. Streak greyish-blue. Vitreous to pearly lustre. The plane of the optical axis is the plane of symmetry. Gastaldite exhibits negative double refraction, an inclined dispersion and strong pleochroism. An analysis showed it to have the following percentage composition.

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
58·55	21·40	9·04	3·92	2·03	4·77	trace = 99·71

from which the formula $3RO.2Al_2O_3.9SiO_2$ is obtained, $RO = FeO, Na_2O, MgO, CaO$. Gastaldite occurs in chloritic slate, in the valley of Aosta, near Brozzo, and also in the valley of Locano, accompanied by copper-pyrites, iron-pyrites, garnet and apatite. C. A. B.

The Kaolin of the Thuringian Variegated Sandstone. By E. Schmid (*Jahrb. f. Min.*, 1876, 669—670).—The kaolin-bearing rocks of the Thuringian variegated sandstone belong to the central portion of this formation. A microscopical examination of the coarse residuum after levigation showed it to consist of mica lamellæ, fragments of quartz, and small, broad, crooked, diagonally striated or indented prisms (microvermiculite). In addition to these were narrow prisms resembling tourmaline (microschörlite). The finer levigated portion was similarly constituted, and a sample from Eisenberg furnished on analysis the formula $R_2O_2 + 2SiO_2 + 2H_2O$, which corresponds with that of kaolin from Ane and other localities. These crude kaolins are mixtures of kaolin with from 6 to 26 per cent. of quartz dust and secondary silicates, such as those already mentioned above.

C. A. B.

The Occurrence of Chromite in Serpentine. By A. HELLAND (*Jahrb. f. Min.*, 1876, 670—671).—In Norway it occurs only in serpentine as in other countries, the two best localities being in the neighbourhood of Roerras. The chromite-bearing serpentine does not belong to any particular formation, but occurs in the middle of the slaty rocks, on the borders of the latter with sparagmite rock. The occurrence of chromite and serpentine is independent, however, of a stratified formation, as the latter mineral is oftener found in "points" or mounds than in strata. These "points" are characterized by a reddish-brown colour, an absence of vegetation, and accumulation of large masses or blocks at their bases. The reddish-brown colour is only superficial, the interior of the rock being dark-green in colour, translucent on the edges, with a splintery fracture. Accessory to the ordinary serpentine were precious serpentine, picrolite, chrysotile, talc, grammatite, magnesite, and above all chromite, the latter occurring in veins, bands, lenses, and reniform masses, often accompanied by magnetite. Nests of chromite occur occasionally in a row, one behind the other in the direction of the strike. The serpentine rock is very often penetrated by clefts, filled up with minerals having a composition similar to that of serpentine, appearing sometimes older or younger than the ore. The thickness of the deposits of ore is very variable; generally speaking, it increases with the size of the serpentine mass. The author found diallagite to be a common accessory of the serpentine rock, from which he concludes that the latter was derived from a diallagite-bearing rock, as it is a well-known fact that diallagite often contains chromite. The decomposition of diallagite would result in the deposition of chromite, and the carrying away of the greater part of the constituents, magnesium silicate alone remaining; and this was finally converted into serpentine by taking up water. The change of volume probably caused the clefts observed. C. A. B.

Constitution of Chrome Iron Ore. By A. CHRISTOMANOS (*Deut. Chem. Ges. Ber.*, x, 343—350).—The paper gives the numerical results of the analyses of 50 different specimens of chrome iron ore, from named localities in Greece and Asia Minor. The composition of the specimens may be referred to four types, respectively represented by the formulæ, $Cr_2O_3.2FeO$; $2Cr_2O_3.3FeO$; $Cr_2O_3.FeO$; $3Cr_2O_3.2FeO$.

R. R.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

X.—*Transformation of Aurin into Rosaniline.*

By R. S. DALE, B.A., and C. SCHORLEMMER, F.R.S.

IN our paper on aurin (this Journal, 1873, 434) we shortly mentioned a red colouring matter called peonin or red aurin, which is formed by the action of ammonia on aurin. This compound contains nitrogen, and yields, when heated with solid caustic potash a distillate containing aniline. When red aurin is heated with alcoholic ammonia for several days to 150°, the red colour of the solution disappears, and a yellow liquid is obtained, which on the addition of water deposits a white crystalline precipitate. This body possesses all the characteristic properties of rosaniline; it dissolves in acetic acid with a splendid crimson colour, and yields with strong hydrochloric acid a dark yellow solution, which on the addition of water becomes red. It dyes wool and silk the same shade, and under exactly the same conditions as pure magenta does, and fixes on cotton mordanted with antimony tannate like this colour. The formation of this colouring matter from aurin is explained by the equation—

$$C_{20}H_{14}O_3 + 3NH_3 = C_{20}H_{17}N_3 + 3H_2O.$$

According to Hofmann, however, rosaniline has the composition $C_{20}H_{19}N_3$, and Caro and Wanklyn converted it (1866), by means of the diazo-reaction, into rosolic acid, which, as Caro and Graebe have shown (1873), has the formula $C_{20}H_{16}O_3$, while aurin has undoubtedly the formula $C_{20}H_{14}O_3$. A careful investigation of our base and its salts will clear up these points; we will only here remark that, in analyses of organic colouring matters, the percentage of hydrogen is often found too high. An example of this kind is offered by Schunck's classical research on alizarin, which he carefully analysed, and found that the results agree best with the formula $C_{14}H_{10}O_4$, instead of $C_{14}H_8O_4$.

In comparing the absorption-spectrum of the hydrochloride of our base with that of pure rosaniline hydrochloride, we found them quite identical.

We have transformed our rosaniline, not only into Hofmann's violet and aniline-blue, but also into aniline-green, obtaining at the same time the violet, which is always produced in the formation of the green.

When aurin is heated with alcoholic ammonia for several days to 150°, the rosaniline which is first formed is converted into *leucaniline.* This is readily explained: the alcohol in presence of an alkali acts as a reducing agent. But from that one might conclude that a similar action took place in the formation of rosaniline from aurin, thus—

$$C_{20}H_{14}O_3 + 3NH_3 + C_2H_6O = C_{20}H_{19}N_3 + 3H_2O + C_2H_4O.$$

But this is not the case, inasmuch as rosaniline is readily formed by heating aurin with aqueous ammonia to 120° for 20 hours. If the temperature be raised to 180—200°, other colourless bodies are formed besides, resembling those which Liebermann obtained by heating rosaniline with water.

We believe that rosolic acid and aurin are identical. One of us, who first investigated the action of nitrous acid on rosaniline, and patented the new colour thus formed, in conjunction with Paraf, examined it after our investigation of aurin, and found that on purifying the crude product by ammonia in the same way as we purified crude aurin, a crystalline ammonia compound is obtained, which after decomposition with an acid and crystallisation from alcohol or acetic acid, yielded crystals which could not be distinguished from aurin. He made a few analyses, which showed that it contained the same amount of carbon as aurin, but the percentage of hydrogen was always found too high. He did not continue this research when he became aware that Caro and Gräbe were engaged in an investigation of the same subject. These two chemists state, in their paper on rosolic acid, that they found it more difficult than they expected to prepare an aurin having exactly the composition $C_{20}H_{14}O_3$, and that they frequently obtained a compound having the formula $C_{40}H_{28}O_7$, but as chief product substances containing still more oxygen were formed. We never found the least difficulty in obtaining pure aurin, which since our last paper we have prepared repeatedly by heating a mixture of sulphuric acid and pure phenol on a water-bath, and adding the oxalic acid only gradually, always waiting until the evolution of gas ceased, and not using sufficient to attack all the phenol.

Zulkowsky has lately published a paper on "The Constituents of Corallin" (*Deut. Chem. Ges. Ber.*, x, 460), in which he says that crude corallin (aurin) contains so large a quantity of a pale red resinous body, that it is difficult to understand how it could hitherto have been overlooked. The existence of this body, which in the pure state is perfectly colourless, has been known to us since the commencement of our researches, and we then stated that commercial aurin was a mixture of several bodies. Besides the white resin, it also contains a dark red colouring matter, which is not only much more soluble in alcohol than aurin, but also increases the solubility of the latter, which can be obtained pure only by a number of re-crystallisations. None of these bodies is formed by preparing aurin according to the method which we have just described, and its formation from phenol and oxalic acid, as well as that from phenol and salicyl-aldehyde, lead to the formula $C_{20}H_{14}O_3$.

XI.—*On Primary Normal Heptyl Alcohol and some of its Derivatives.*

By Charles Fred. Cross, Student at the Owens College.

This alcohol was first prepared by Grimshaw and Schorlemmer by reduction from oenanthol, according to the method of Lieben and Rossi (*Journ. Chem. Soc.* [2], xi, 1873). Schorlemmer subsequently showed that this method, although successful when applied to the reduction of aldehydes lower in the series, is but very partially so in the case of oenanthol. The cause of its failure lies most probably in the imperfect solubility of this aldehyde in water. In support of this view I may cite the experiments of Friedel, in which he showed that, while the action of nascent hydrogen upon acetone in aqueous solution results in the almost exclusive production of isopropyl alcohol, by adding potassium carbonate to the water employed, and thereby bringing about only a partial solution of the acetone, the reaction is so modified that pinakone becomes the chief product, the alcohol being formed in but very small quantity.

Schorlemmer (*Lieb. Ann.*, 177, 303) obtained much better results by dissolving the oenanthol in strong acetic acid, and evolving in this solution the hydrogen necessary for reduction by liquid sodium amalgam. At his request I have undertaken the following investigation, in which I have first endeavoured to determine the conditions under which this reduction may be most favourably effected. Applying the experience thus obtained, I have succeeded in preparing the pure alcohol in considerable quantity, and from the alcohol some of its more important derivatives.

I now proceed to give in detail the results of my investigation, commencing with the preparation of the aldehyde.

Oenanthol, $C_7H_{14}O$.

Castor oil was subjected to an extremely rapid dry distillation, according to the directions of Erlenmeyer and Sigel, and the resulting crude oenanthol purified by fractional distillation. The greater portion boiled between 150° and 160°. In order to observe its specific gravity and boiling point, still a vexed question, some quantity of this fraction was further fractionated, and the pure aldehyde obtained. Its sp. gr. at 16° was 0·823, and its boiling point was 152°,* under the barometric pressure 748·6 mm.

The purity of the product is evident from the subjoined analysis.

0·2047 yielded, on combustion with copper oxide and oxygen, 0·223 H_2O and 0·552 CO_2.

	Calc.		Found.
C_7	84	73·68	73·73
H_{14}	14	12·28	12·11
O	16	14·04	—
		100·00	

Heptyl Alcohol, $C_7H_{15}.OH$.

Numerous experiments were tried with a view to determine the proportion of acetic acid which may be most advantageously employed; the best results were obtained with an acid of 65 per cent. At this strength, while effectually holding the aldehyde in solution, it prevents a too rapid disengagement of hydrogen from the sodium amalgam, which was employed as the reducing agent. For the purposes of reduction 15 grams were dissolved in 150 grams of the dilute acid, and treated in a loosely corked bottle with 10 grams of sodium, previously amalgamated with about 1,000 grams of mercury, and added in successive small portions, several such quantities being taken. About ten days were required for complete reduction.

At the completion of the process, the upper stratum of liquid which had separated out was drawn off, washed, and left for some time over fused potassium carbonate. The lower stratum still contained a large quantity of alcohol, which was separated by neutralizing the excess of acetic acid with sodium carbonate; from the concentrated solution of sodium acetate the alcohol separated out, and was drawn off and treated as before. Finally on distilling the saline solution a residuum of alcohol passed over with the vapour of water and was easily removed. These several portions were now collectively purified by fractional distillation. When the thermometer had risen to 180° the distillation was stopped, and the residue, of which a considerable quantity remained, was boiled for some time with a weak solution of potash. The whole was then transferred to a retort and distilled. A large quantity of alcohol previously present in the residue as acetate was thus obtained and purified as before.

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* All the boiling points given in this paper were determined by the same thermometer which Schorlemmer used in his researches; the mercury column being entirely enveloped with vapour.

In reference to yield, I may add that from 300 grams of the impure aldehyde I obtained in this way 180 grams of the impure alcohol, which yielded on purification 120 grams of the fraction boiling from 170—180°, therefore, of the practically pure alcohol.

In order to observe the physical properties of the alcohol, some quantity of this fraction was purified by repeated rectification over small portions of metallic sodium. Thus obtained the pure alcohol is a colourless liquid, possessing an agreeable pear-like odour. Its sp. gr. was determined at three temperatures, with the subjoined results:—

At 0°	0·838
„ 16°	0·830
„ 27°	0·824

These numbers express the relation to distilled water at the same respective temperatures.

Under the bar. pressure 764·1 mm., the boiling point of the alcohol is 175·5°. (Under identical conditions water boiled at 100·5°.) On combustion with copper oxide and oxygen, 0·1768 yielded 0·2175 H_2O and 0·4685 CO_2.

	Calc.		Found.
C_7	84	72·42	72·23
H_{16}	16	13·79	13·67
O	16	13·79	—
	116	100·00	

Heptyl Chloride, $C_7H_{15}Cl$.

This compound was obtained by saturating the alcohol, cooled in a freezing mixture, with hydrochloric acid gas (for the preparation of this, as of the succeeding compound, the fraction boiling between 170—180° was employed), and subsequently heating with the concentrated aqueous acid to 120—130° in a sealed tube. The impure product was washed with distilled water, dried over calcium chloride, rectified from a small quantity of phosphorus pentachloride, and finally purified by fractional distillation.

The chloride was thus obtained as a colourless liquid, of sp. gr. 0·881 at 16°, and boiling, under the bar. pressure 754 mm., at 159·2°.

The determination of the chlorine gave the subjoined result:—

0·210 yielded 0·224 AgCl.

	Calc.	Found.
Percentage chlorine	26·39	26·43

Heptyl Bromide, $C_7H_{15}Br$.

The details of the preparation of this compound are similar to the preceding.

It is a colourless liquid, of sp. gr. 1·133 at 16°, and boiling under the bar. pressure 750·6 mm. at 178·5°. The determination of the bromine gave the following results :—

(1.) 0·217 yielded ·225 AgBr.
(2.) 0·1446 „ ·1515 „

	Calc.		Found.
Percentage bromine......	44·69	(1)	44·20
		(2)	44·64

Heptyl Iodide, $C_7H_{15}I$.

Preparation essentially the same as that of the chloride. It is a colourless liquid, of sp. gr. 1·346 at 16°. Under the bar. pressure 754·8 mm. its boiling point is 201°.

The determination of the iodine gave the following results :—

·2334 yielded ·240 AgI.

	Calc.	Found.
Percentage iodine..........	56·19	55·86

Heptyl Acetate, $\left.\begin{matrix}C_7H_{15}\\C_2H_3O\end{matrix}\right\}O$.

This compound was prepared by heating the iodide with potassium acetate and glacial acetic acid in a sealed tube to 180°. It is remarkable that below 170° only a very partial decomposition of the iodide takes place, a fact which I have observed to hold generally for similar decompositions of the halogen compounds of this radical.

The acetate was separated by pouring the contents of the tube into a solution of calcium chloride, drawn off, washed, dried, and purified by fractional distillation.

Thus obtained the acetate is a colourless liquid, possessing an extremely agreeable fruity smell. Its sp. gr. at 16° is 0·874. Under a bar. pressure of 758·5 mm. its boiling point was found to be 191·5°.

On combustion with copper oxide and oxygen ·120 yielded ·121 H_2O and ·300 CO_2.

	Calc.		Found.
C_9	108	68·35	68·18
H_{18}	18	11·39	11·20
O_2	32	20·26	—
	158	100·00	

Heptyl Oenanthylate, $\left.\begin{matrix} C_7H_{15} \\ C_7H_{13}O \end{matrix}\right\} O$.

To prepare this compound the iodide was heated with silver oenanthylate (prepared from oenanthol in the usual way) at first in a water-bath, and finally for some time in an oil-bath at 180°. When the reaction was quite complete the temperature of the latter was slowly raised. At 260° the contents of the flask began to boil, and between 270—290° an oily liquid distilled. This was purified by fractional distillation.

Thus obtained this compound is a colourless oily liquid, possessing a faint, disagreeable, fatty odour.

At 16° its sp. gr. was found to be 0·870. Under the bar. pressure 760 mm. its boiling point is 270—272°. On combustion with copper oxide—

·207 gave ·555 CO_2 and ·2315 H_2O.

	Calc.		Found.
C_{14}	168	73·68	72·94
H_{28}	28	12·28	12·42
O_2	32	14·04	—
	228	100·00	

Heptyl Ethyl Ether, $\left.\begin{matrix} C_7H_{15} \\ C_2H_5 \end{matrix}\right\} O$.

As a result of two unsuccessful attempts to prepare heptylamine by the action of potassium cyanate upon the iodide and decomposition of the resulting cyanic ether by distillation with potassium hydrate, a liquid was obtained separating as an ethereal layer upon the surface of the dilute acid in the receiver. This was drawn off, dried, and purified by fractional distillation. A colourless liquid was thus obtained, having a faint citron-like odour. Its sp. gr. at 16° was 0·790; under a bar. pressure of 748·3 mm. it boiled at 165°. On combustion with copper oxide—

·2085 gave ·5695 CO_2 and ·2605 H_2O.

	Calc.		Found.
C_9	108	75·00	74·48
H_{20}	20	13·89	13·86
O............	16	11·11	—
	144	100·00	

In order finally to verify this liquid as the ethylic ether, the iodide was heated with sodium ethylate to 180° in a sealed tube. On pouring the contents of the tube into water a liquid was separated as an ethereal layer, which was dried and purified by fractional distillation. The odour of this liquid was precisely similar to that of the preceding; further, at 16° its sp. gr. was found to be ·791, and under the bar. pressure 755 mm. it boiled at 166—167°. No doubt therefore remains as to the identity of the two liquids.

In conclusion I would call attention to the general coincidence of the boiling points of the primary normal heptyl compounds observed by me with those calculated for the same by Schorlemmer (*Chemistry of the Carbon Compounds*, p. 38). This will be evident from the following table:—

	Boiling points.	
	Calculated.	Observed.
Heptyl chloride	158°	159·2°
„ bromide........	179°	178·5°
„ iodide...........	202°	201·0°
„ acetate	189°	191·5°

XII.—*On Certain Bismuth Compounds.* Part VI.

By M. M. Pattison Muir, F.R.S.E.,
Assistant Lecturer on Chemistry, The Owens College.

1. In part IV of the present series of papers I endeavoured to sketch a few of the general relations existing between the hydrates of bismuth and between these and the corresponding oxides. I incidentally mentioned a qualitative reaction of bismuthous oxide (Bi_2O_3) which, it seemed to me, was best explained on the hypothesis of the existence of hypobismuthous oxide (Bi_2O_2). In a short note, since communicated to the Society, I showed how the formation of this lower oxide of bismuth may be applied to the detection of very small quantities of the metal. I now propose to communicate some further details with regard to the preparation and properties of this lower oxide.

2. The history of the researches into the existence and nature of an oxide of bismuth containing less oxygen than bismuthous oxide (Bi_2O_3) is briefly as follows:—

Thomson (*Proc. Glasgow Phil. Soc.*, 1841–42, p. 4) mentioned the fact that a grey powder is formed when metallic bismuth is gently warmed in the air. He endeavoured to separate this powder from unoxidised metal by means of a sieve. Heintz endeavoured to prepare an oxide of bismuth which should contain less oxygen than 3 atoms to 2 of metal by heating basic bismuth oxalate to 200° out of contact with air (*Pogg. Ann.*, lxiii, 55); by heating basic bismuth phosphate mixed with microcosmic salt in hydrogen (*ibid.*, lxiii, 559, *et seq.*), and by the attempted reduction of the trioxide in a mixture of carbon monoxide and dioxide (*ibid.*, lxiii, 559, *et seq.*). In the first case Heintz obtained what he believed to be a mixture of bismuth carbonate and metallic bismuth; in the second experiment metallic bismuth containing phosphorus was obtained, and in the third experiment no alteration ensued (see par. 3).

Schneider (*Pogg. Ann.*, lxviii, 49) attempted to prepare the wished-for oxide by reducing bismuth tartrate in hydrogen, also by reducing the double sulphate of bismuth and potassium in hydrogen. The results were in both cases unsatisfactory, although it appeared very probable that a suboxide of bismuth was produced.

Arppe (*Pogg. Ann.*, lxiv, 237) found that digestion of grape sugar and bismuth nitrate solutions, made alkaline with caustic potash, resulted in the production of what appeared to be a mixture of bismuthous oxide or suboxide and metallic bismuth. This experiment was repeated by Schneider (*Pogg. Ann.*, lxviii, 51), making use of a neutral solution of bismuth tartrate in place of bismuth nitrate; he found that metallic bismuth was alone produced. The observation of Berzelius (*Lehrbuch*, ii, 573), that a suboxide of bismuth is formed in the decomposition of water when the negative pole consists of metallic bismuth, does not appear to have been subjected to the test of sufficiently rigid experiment.

Vogel (*Kastner's Archiv.*, xxiii, 86), by digesting basic bismuth nitrate with excess of stannous chloride in closed vessels, obtained a black powder which readily burned to yellow oxide of bismuth when heated in air. According to Berzelius (*Lehrbuch*, ii, 574), this powder contained tin in addition to a suboxide of bismuth.

Schiff (*Ann. Chem. Pharm.*, cxix, 331, *et seq.*) examined more in detail the action of stannous chloride upon basic bismuth nitrate, and found that the first product is an ochre-coloured salt containing tin, bismuth, and oxygen; to this salt Schiff assigned the formula $SnBi_4O_6$. When this compound was heated in air its colour changed to straw-yellow, and it now had the composition $SnBi_4O_8$. Schiff also found that these tin salts might be produced by employing bismuthous oxide in place of the basic nitrate. When the first-named salt was treated with warm caustic potash-solution, in absence of air, Schiff found that the stannic oxide was withdrawn, while a black powder containing bismuth, but other than metallic bismuth, remained. The general reactions of this salt show that it was really hypobismuthous oxide.

Schneider (*Pogg. Ann.*, lxiii, 53, *et seq.*) showed that bismuthous oxide is transformed by the action of tartaric acid and caustic potash into a soluble double tartrate of bismuth and potassium (neither water nor caustic alkali causes a precipitate in neutral solutions of this tartrate); that from stannous oxide, by similar means, a double tartrate of tin and potassium may be formed; that these double tartrates react upon each other with the production of a salt containing bismuth, stannic acid, and tartaric acid, which is soluble in caustic potash; and that from this solution certain salts, especially sodium carbonate, sulphate, and chloride, throw down a precipitate consisting of $SnBi_2O_4.6H_2O$.

By using a solution of stannoso-stannic oxide (Sn_2O_3), in tartaric acid and caustic potash, in place of a similar solution of stannous oxide, and proceeding in a manner similar to that detailed above, Schneider obtained the salt $Sn_2Bi_2O_6.4H_2O$. Schneider found that hot caustic potash only partially withdrew the stannic oxide from these salts.

By preparing a neutral solution of potassium bismuth tartrate, and adding a dilute and slightly alkaline solution of stannous chloride in caustic potash, nearly neutralising excess of potash by means of dilute sulphuric acid, allowing the precipitate to settle out of contact with air, decanting the supernatant liquid, dissolving the precipitate in caustic potash, and removing tartaric acid by addition of sodium carbonate, Schneider obtained a black precipitate containing tin, bismuth, and oxygen, from which strong potash ley completely removed the stannic oxide, leaving pure hypobismuthous oxide. The last-mentioned series of reactions was carried out with cold solutions.

Finally, Schneider (*loc. cit.*) succeeded in preparing pure hypobismuthous oxide by dissolving 1 equiv. of bismuthous oxide along with 1 equiv. of stannous chloride in hydrochloric acid, pouring the solution into tolerably concentrated caustic potash, and washing the black precipitate so produced repeatedly with cold potash ley.*

3. I prepared a quantity of hypobismuthous oxide by the last-mentioned method of Schneider. The process is easily carried out. Care should be taken to conduct the washing with potash-solution in a stoppered flask which should be nearly filled with liquid.

The oxide was dried in a vacuum over sulphuric acid. It presented the appearance of a black, non-metallic, finely-crystalline powder. I did not find that this oxide takes up oxygen so readily as Schneider's account would lead me to suppose. When exposed to air in the moist state it slowly passes into the white hydrate, ($Bi_2O_3.2H_2O$). When dried as described, hypobismuthous oxide is perfectly stable in the air for a very considerable period. The following data give more exact information concerning the oxidation of the dry salt.

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* I have entered into these historical details because I cannot find a clear account of the various methods of preparation of hypobismuthous oxide in any of the textbooks.

0·725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 160° for 3 hours, underwent no increase in weight.

0·725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 180—190° for 1 hour, gained 0·009 gram.

0·725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 180—190° for 3 hours, gained 0·0185 gram.

0·725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 180—190° for 5 hours, gained 0·0205 gram.

0·725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 210—220° for 1½ hours, gained 0·022 gram.

The amount of oxygen which 0·725 gram of Bi_2O_2 must absorb in order to be converted completely into Bi_2O_3 is 0·0266 gram.

Stating the above results in another way, we find that—

After being heated to 180° for 1 hour Bi_2O_2 absorbed 3·76 per cent. of the total oxygen required to convert it into Bi_2O_3.

After being heated to 180° for 3 hours Bi_2O_2 absorbed 69·55 per cent. of the total oxygen required to convert it into Bi_2O_3.

After being heated to 180° for 5 hours Bi_2O_2 absorbed 77·07 per cent. of the total oxygen required to convert it into Bi_2O_3.

After being heated to 210—220° for 1½ hours Bi_2O_2 absorbed 82·71 per cent. of the total oxygen required to convert it into Bi_2O_3.

The colour of the oxide began to change very slowly at 180°; at the close of the operation the great mass of the salt had assumed the light yellow colour of bismuthous oxide, but the outer layers were still for the most part only blackish-yellow. When hypobismuthous oxide is heated over a Bunsen-flame it is at once changed into bismuthous oxide. This change is not attended with any phenomenon which can be described as glowing or burning, which words have been used to describe the change by Vogel and others.

4. Hypobismuthous oxide is easily reduced to metallic bismuth by heating on charcoal in the inner blowpipe flame; the salt is likewise readily and completely deoxidised by heating in hydrogen or in carbon monoxide. Bismuthous oxide is also reduced to metal by heating in carbon monoxide: there appear to be some discrepancies in the statements made concerning this reaction. (See Gmelin's *Handbuch*, ii, 848, and Heintz, *loc. cit.*) Heated in carbon dioxide, hypobismuthous oxide is converted into a greyish-green powder which slowly passes into a yellow-green and finally into a yellow substance. The process is evidently one of slow oxidation.

5. The action of a tolerably concentrated boiling solution of caustic

potash upon the oxide results in the production of metallic bismuth. Hot dilute hydrochloric acid partially dissolves this oxide; the insoluble portion consists of metallic bismuth. Dilute sulphuric acid has a similar action; a much smaller quantity, however, of the salt passes into solution. Dilute nitric acid dissolves hypobismuthous oxide with great ease.

6. This oxide of bismuth is readily converted into the higher oxides by boiling with caustic potash and a little bromine; the final product of the reaction is bismuthic oxide, or rather hydrate, $Bi_2O_5.xH_2O$. I find that the same reaction serves to convert bismuthous oxide, and even metallic bismuth itself, when finely powdered, into bismuthic hydrate This method for preparing that salt is much easier and quicker than the ordinary method in which chlorine is used as an oxidiser. It is only necessary to heat bismuthous oxide with strong potash ley, to add bromine slowly, and finally to boil for a few minutes in order to obtain a good yield of the red hydrate. The product of the action is washed with water, warmed with concentrated nitric acid, and again washed free from acid.

I did not consider it necessary to perform a quantitative analysis of hypobismuthous oxide, inasmuch as there can be no doubt, from the general reactions of the salt, that the substance obtained by me was identical with that obtained by Schneider, who has given a large number of analyses all leading to the formula Bi_2O_2.

7. In the fourth part of my papers on bismuth-compounds I have endeavoured to generalise some of the properties of the hydrates and oxides of bismuth, and to express these generalisations in appropriate formulæ. According to the formulæ therein given the passage from bismuthic to hypobismuthous oxide consists in a gradual drawing together of the bismuth atoms with simultaneous expulsion of oxygen atoms. I have shown that bismuthic oxide begins to suffer deoxidation at 150°, hypobismuthic oxide at 250°. It is known that bismuthous oxide is stable at a red heat; the fact that this oxide loses oxygen when heated in carbon monoxide, and also, as mentioned in part iv, when heated in an atmosphere of such reducing gases as are produced by the slow ignition of paper, shows that bismuthous oxide is more ready to part with oxygen than it is to pass into a higher state of oxidation. I have now shown that hypobismuthous oxide begins to absorb oxygen at a temperature of about 180°, but that the process of oxidation is slow at this temperature, also that this oxide parts with the whole of its oxygen without any great difficulty. The most stable oxide of bismuth is therefore evidently bismuthous oxide, Bi_2O_3; in this respect bismuth differs from phosphorus. The points of agreement and difference between the oxides and hydrates of the members of the nitrogen series is a subject of much interest. I

shall defer what I have to say upon this subject until I am in a position to discuss the general relations holding good between the members of the series.

8. I have already referred to the salts containing tin, bismuth, and oxygen obtained by Schiff and by Schneider. Schiff's salt, No. 1, has the empirical formula $SnBi_4O_6$: I would suggest that very probably this substance is the dibismuthyl salt derived from that hydrate of tin which corresponds with the oxide SnO. When the salt is heated it absorbs oxygen and becomes $SnBi_4O_8$; this salt I would regard as the normal bismuthyl salt of the hydrate corresponding to stannic oxide (SnO_2). In the same way Schneider's salts may be viewed (1) as the normal bismuthyl salt of the hydrate $Sn(OH)_2$; (2) as the acid bismuthyl salt of the hydrate, $Sn_2(OH)_6$.

I have formulated these salts below—

Oxide of tin.	Bismuth salt.	Hydrate of tin.
SnO	Schiff's No. 1. $Sn(OBi_2O_2)_2$	$Sn(OH)_2$

I have ventured to give the name of *dibismuthyl* to the group Bi_2O_2 when in combination—

Oxide of tin.	Bismuth salt.	Hydrate of tin.
SnO_2	Schiff's No. 2. $Sn(OBiO)_4$	$Sn(OH)_4$
SnO	Schneider's No. 1. $Sn(OBiO)_2.6H_2O$	$Sn(OH)_2$
Sn_2O_3	Schneider's No. 2. $Sn_2(OBiO)_2(OH)_4.2H_2O$	$Sn_2(OH)_6$

9. In a paper communicated to the Society (*Chem. Soc. Jour.*, vol. ii, 1876, p. 12) I have shown that in the sublimation of bismuthous bromide, in a retort or other confined space of air, an oxybromide having the composition $Bi_8Br_6O_{15}$ is produced. If bismuthous chloride be slowly sublimed under similar conditions an oxychloride is produced; but this salt is not the analogue of the oxybromide just mentioned.

A quantity of bismuthous chloride was placed in a large watch-glass which was covered with another of the same size; the lower glass was very gently warmed during the space of about an hour. Well-defined crystals of the trichloride were obtained on the upper watch-glass, while a reddish-yellow highly crystalline powder remained in the lower. This powder was washed with water, whereby any undecomposed chloride was readily separated as BiOCl, the new oxychloride settling quickly to the bottom of the washing vessel: the residue was dried at 90—100° and analysed—

(1) 0·519 gram gave 0·467 gram Bi_2O_3 = 0·4191 gram Bi.
(2) 0·519 „ „ 0·469 „ „ = 0·4209 „ „
(3) 0·519 „ „ 0·281 „ AgCl = 0·06952 „ Cl.
(4) 0·519 „ „ 0·283 „ „ = 0·0701 „ „

	Found.					Calculated for $Bi_3Cl_3O_2$.
	I.	II.	III.	IV.	Mean.	
Bismuth	80·73	81·09	—	—	80·91	81·98
Chlorine	—	—	13·39	13·51	13·45	13·86
Oxygen (by difference)	—	—	—	—	5·64	4·16
					100·00	100·00

The results agree approximately with the formula $Bi_3Cl_3O_2$. I will give further analyses of the same salt in the sequel.

10. It is evident from this result, and from that already cited, that bismuthous bromide, when melted in presence of air, takes up a proportion of oxygen much larger than that which enters into combination with bismuthous chloride under similar conditions. The fact that the bromide is more readily oxidised than the corresponding chloride is also illustrated by the behaviour of hot bismuthous oxide towards chlorine and bromine respectively. The action of chlorine results in the formation of bismuthous chloride, that is to say, the chlorine exerts a deoxidising influence; the action of bromine results in the production of an oxybromide of bismuthyl, viz., $(BiO)_{11}Br_7O_2$ (*Chem. Soc. J.*, vol. i, 1876, pp. 26—27). The greater readiness to take up oxygen exhibited by bismuthous bromide, as compared with the corresponding chloride, is in keeping with the general behaviour of the bromides and chlorides respectively.

11. Geuther and Michaelis (*Deut. Chem. Ges. Ber.*, iv, 76) have shown that the action of nitrogen trioxide or tetroxide upon phosphorous chloride results in the production of pyrophosphoryl chloride, $P_2O_3Cl_4$, and nitrosyl chloride, NOCl. Weber (*Pogg. Ann.*, cxxiii, 347) has described the properties of a compound of antimonic chloride and nitrosyl chloride, $SbCl_5NOCl$, obtained by treating the first-named salt with nitrogen tetroxide.

From a consideration of the formulæ and general behaviour of the bismuth chlorides, bromides, oxychlorides, and oxybromides, as compared with the corresponding phosphorus salts, I did not consider it probable that pyrobismuthyl chloride, $Bi_2O_3Cl_4$, would be formed by the action of nitrogen trioxide or tetroxide upon bismuthous chloride; it was more likely that oxidation would not be carried far enough to produce this salt.

A quantity of bismuthous chloride was heated to fusion in a small inverted retort, the beak of which was connected with a U-tube kept cool by being surrounded with a mixture of salt and ice. The vapours produced by heating together starch and moderately concentrated nitric acid were passed into the retort. So soon as the nitrous vapours came into contact with the fused mass, the latter appeared to enter into violent ebullition; the retort became very warm; after a few minutes the contents of the retort had solidified to a reddish-yellow, compact, hard, crystalline mass. This mass was washed into a mortar, ground up with water, repeatedly washed with the same liquid, and finally dried at 90—100°. The washing with water showed that only a very small quantity of bismuthous chloride remained undecomposed after the reaction. The U-tube contained a quantity of a greenish-brown liquid, which, when mixed with water, gave the reactions for chlorine and nitrous acid: the liquid most probably contained nitrosyl chloride.

The salt dried at 90—100° was analysed.

(1) 0·2658 gram gave 0·247 gram Bi_2O_3 = 0·2216 gram Bi.
(2) 0·2658 „ „ 0·245 „ „ = 0·2199 „ „
(3) 0·8156 „ „ 0·744 „ „ = 0·6677 „ „
(4) 0·8156 „ „ 0·740 „ „ = 0·6641 „ „
(5) 0·2658 „ „ 0·145 „ AgCl & 0·003 gram Ag = 0·0367 gram Cl.
(6) 0·8156 „ „ 0·442 „ AgCl & 0·0025 gram Ag = 0·1099 gram Cl.
(7) 0·8156 „ „ 0·4475 „ AgCl & 0·0015 gram Ag = 0·1110 gram Cl.
(8) 0·8156 „ after precipitation of bismuth as carbonate, required 48 cb.c. standardised silver nitrate solution for complete precipitation of chlorine = 0·1099 gram Cl.

(1 cb.c. $AgNO_3$ solution = 2·29 mgm. Cl).

	Found.					
	I.	II.	III.	IV.	V.	VI.
Bismuth............	83·37	82·72	81·86	81·42	—	—
Chlorine............	—	—	—	—	13·70	13·47

	VII.	VIII.	Mean.	Calculated for $Bi_3Cl_3O_2$.
Bismuth............	—	—	82·34	81·98
Chlorine............	13·61	13·47	13·56	13·86
Oxygen (by difference)	—	—	4·10	4·16
			100·00	100·00

12. The numbers obtained in the foregoing analyses, although agreeing very well with those required by the formula $Bi_3Cl_3O_2$, can, nevertheless, be interpreted by assigning one or other of the three following formulæ to the salt:—

	$Bi_4Cl_4O_3$.	$Bi_5Cl_5O_4$.	$Bi_7Cl_7O_6$.
Bismuth	81·51	81·30	81·01
Chlorine	13·78	13·24	13·69
Oxygen...........	4·71	5·46	5·30
	100·00	100·00	100·00

Taking the mean of all the analyses of the salt, including those detailed in par. 9, we have the following result:—

Bismuth	81·86
Chlorine	13·53
Oxygen	4·61
	100·00

These results agree equally well with the formula $Bi_3Cl_3O_2$ and with $Bi_4Cl_4O_3$.

If the salt has the composition expressed by the former formula, it may, perhaps, be regarded as *bismuthic bismuthyl chloride*, $Bi(BiO)_2Cl_3$; if the composition expressed by the latter formula, as a compound of *bismuthous oxide* and *hypobismuthous chloride*, $Bi_2O_3.Bi_2Cl_4$; or as a derivative of bismuthous chloride in which chlorine is partly replaced by the group Bi_2O_3, viz., $Bi_2\left\{\begin{matrix}Cl_4\\Bi_2O_3\end{matrix}\right.$.

The reaction, $3BiCl_3 + 3N_2O_3 = Bi_3Cl_3O_2 + 6NOCl + O$, or
The reaction, $4BiCl_3 + 4N_2O_3 = Bi_4Cl_4O_3 + 8NOCl + O$,

may, perhaps, represent the production of the oxychloride from bismuthous chloride.

13. Whatever be the formula assigned to this oxychloride, the results of analyses, as well as the general properties of the substances, show that the salt produced by fusing bismuthous chloride in a confined space of air, is the same as that formed by the action of nitrogen trioxide upon the same chloride in the state of fusion. The oxidation is carried no further in the one case than in the other. In the case of phosphorous chloride, the result is different. This salt absorbs oxygen at a boiling temperature, giving $POCl_3$, but is converted by N_2O_3 into $P_2O_3Cl_4$: in each case, the oxidation is more complete than with the corresponding chloride of bismuth, and the latter oxidation is more complete than the former.

14. The new oxychloride of bismuth is insoluble in, and is not acted upon by, water: exposed to the air for days, it undergoes no change: it is soluble in hot hydrochloric or nitric acid, but is less readily dissolved by hot sulphuric acid. When boiled with caustic soda solution, the whole of the chlorine is slowly removed and is found in the liquid, while a yellowish-white residue, free from chlorine, remains undissolved: this residue appears to consist of bismuthous oxide. When heated over the Bunsen lamp, the oxychloride suffers no change; at an incipient white heat it is fused to a yellowish pasty mass, while white fumes are evolved: the residue contains a considerable quantity of chlorine, and appears to consist for the most part of undecomposed oxychloride.

A quantity of the salt was gently heated in dry hydrogen; it readily underwent change, the colour first becoming reddish-brown, then black. The black salt appeared to preserve the crystalline form of the original substance: one preparation was found to contain 25·26 per cent. of chlorine, another, 9·16 per cent., and 85·1 per cent. of bismuth. The escaping hydrogen evidently contained suspended matter; when conducted into water, it produced a milkiness in that liquid, and after some time a white precipitate which contained bismuth and chlorine; the water simultaneously acquired a slightly acid reaction. The final product of the action of hydrogen upon this oxychloride is metallic bismuth.

15. In order to compare the action of nitrogen trioxide upon bismuthous chloride with that of the same substance upon the corresponding bromide, I submitted a quantity of the latter salt to the action of the fumes produced by heating starch with moderately concentrated nitric acid, under conditions exactly similar to those detailed in par. 11. The phenomena presenting themselves to the eye were very similar to those described in the paragraph referred to. A liquid was obtained in the U-tube, showing the reactions for bromine and nitrous acid. A light yellowish-grey, crystalline powder, which was unacted upon by water, was formed in the retort. Complete decomposition of the bismuthous bromide was effected by the nitrous fumes. The solid product of the action was washed with water, dried at 90—100°, and analysed.

(1) 0·2465 gram gave 0·1935 gram Bi_2O_3 = 0·1736 gram Bi.

(2) 0·648 ,, ,, 0·315 ,, AgBr = 0·134 ,, Br.

	Found.			Calculated for
	I.	II.	III.	$Bi_8Br_6O_{15}$.
Bismuth	70·43	—	—	70·00
Bromine...........	—	20·68	—	20·00
Oxygen (difference)	—	—	8·89	10·00

The general behaviour of this oxybromide, as well as the results of analysis, leave no doubt of the identity of this salt with that produced by fusing bismuthous bromide in contact with air (*Chem. Soc. J.*, vol. ii, 1876, p. 12). Bismuthous bromide then resembles the corresponding chloride in the fact that the action of nitrogen trioxide upon the fused salt produces the same oxy-derivative as is formed by the action of air alone. With the bromide, however, the oxidation is, in each instance, carried further than is the case with the chloride.

16. An attempt to prepare an oxychloride of bismuth analogous to powder of Algaroth ($SbOCl.2Sb_2O_3$), by heating together bismuthic oxide, Bi_2O_5, and bismuthyl chloride, BiOCl, led to negative results. A mixture of Bi_2O_3 and BiOCl only was obtained: the particles of the

two salts could be readily distinguished under a lens: the mixture was of indefinite composition.

17. Michaelis (*Deut. Chem. Ges. Ber.*, v, 9—414, &c.) has shown that phosphorous chloride forms with bromine a bromochloride having the formula PCl_3Br_2: this compound is, however, very unstable, being resolved into free bromine and phosphorous chloride at 35°. The existence of this bromochloride is in keeping with the marked quinquivalent character of phosphorus. I have already described (*Chem. Soc. J.*, vol. i, 1876, p. 144) the unsuccessful attempts which I have made to prepare a chloride of bismuth containing more chlorine than bismuthous chloride. Keeping in mind the apparent fact that the quantivalence of an elementary atom is more or less influenced by the other atoms with which it is united in a molecule, I thought that it might be possible to prepare a bromochloride of bismuth in which bismuth should play the part of a quinquivalent element. Of course, the mere production of a compound having the composition expressed by the formula $nBiCl_xBr_n$, where $x + n = 5$, and where n is any whole number, would not enable us to determine the valency of bismuth. Nevertheless, having proved the actual existence of such a compound, the most simple hypothesis to explain that existence would, I think, be that which regards bismuth as a quinquivalent element.

One might, however, at the outset, almost despair of producing such a compound as that formulated above. Bismuthous chloride is solid at even somewhat high temperatures; it would scarcely be allowable to imagine the formation of a compound by the action of bromine upon the solid chloride: the compound, if produced, would most probably, almost certainly, undergo dissociation at temperatures considerably below the fusing point of bismuthous chloride: in other words, the compound would probably be dissociated before it was actually produced.

Actual experiments led only to negative results.

Bismuthous chloride was melted in a small bulb blown on the end of a long piece of glass tubing; bromine was added in the proportion required by the equation $BiCl_3 + Br_2 = BiCl_3Br_2$, and heating was continued until fumes of bromine nearly ceased to be evolved. The product was a greyish-white, crystalline, very deliquescent mass, which contained bismuth, chlorine, and bromine. Analyses of this substance varied somewhat in their results: thus, 65·47 per cent. of bismuth was found, 4·95 per cent. of bromine, and 30·12 per cent. of chlorine another portion showed 65·1 per cent. of bismuth, 2·88 per cent. of bromine, and 31·13 per cent. of chlorine. A portion of the substance was sublimed from one watch glass into another placed over it: the sublimate consisted of white deliquescent crystals, samples of which showed 65·81, and 64·39 per cent. of bismuth, with from 31 to 32 per cent. of chlorine, and very small quantities of bromine. During the sublimation of the substance, a greyish, crystalline, non-volatile body was formed in the lower watch glass. Analysis, and general behaviour, showed that this was an oxychloride identical in composition with that described in pars. 9, 11, and 12. No bromochloride was produced in the above reaction: the results of analysis agree with the numbers demanded by bismuthous chloride, viz., bismuth 66·35, and chlorine 33·65 per cent.: the chloride evidently contained small varying quantities of mechanically adhering bromine.

18. In the sublimation of bismuthous chloride mixed with bromine, the former salt alone undergoes chemical change: that the bromine should be incapable of replacing chlorine when traces of oxychloride are once formed, was almost to have been expected; but it would not have been very remarkable had the presence of the bromine modified in some way the oxidising action of the air upon the fused chloride. No such modifying influence was however noticed.

19. All attempts to prepare trichloride of bismuthyl, $BiOCl_3$, corresponding with $POCl_3$, have failed. I imagined it might be possible to prepare the sulphur analogue, $BiSCl_3$. In order to test the accuracy of this supposition, I very gently heated bismuthous chloride and sulphur, in the proportion of 1 molecule of the former to 2 of the latter, in a covered crucible for several hours. Colourless crystals, mixed with others of a yellow colour, were then apparent adhering to the lid of the crucible, while a dark-red crystalline substance was found in the crucible itself. This dark-red substance was unacted upon by water; it contained bismuth, chlorine, and sulphur. Estimations of chlorine gave results nearly agreeing with those required by the formula, $BiSCl$. The general properties of the salt were the same as those described by Schneider (*Pogg. Ann.*, xciii, 464) as characterising sulphobismuthyl chloride, $BiSCl$.

The direct action of sulphur upon bismuthous chloride results in the replacement of two chlorine atoms by one sulphur atom. Schneider (*loc. cit.*) has described other methods of preparing sulphobismuthyl chloride; he has also described (*Pogg. Ann.*, xciv, 628) the corresponding salt in which selenium is substituted for sulphur.

XIII. *On a Slight Modification of Hofmann's Vapour-density Apparatus.*

By M. M. Pattison Muir, F.R.S.E., Assistant Lecturer on Chemistry, and S. Sugiura, Chemical Student, in The Owens College.

1. In a recent communication (*Deut. Chem. Ges. Ber.*, ix, 1304) Hofmann has described a method for determining vapour-densities whereby the employment of a graduated barometer-tube is no longer rendered necessary. In working with aniline vapour, or that of some other liquid of high boiling point, a graduated tube is very liable to crack: hence the importance of any device which will do away with the employment of such tubes.

Hofmann's modification of his original process consists in supporting the barometer-tube and mantle on a plate of caoutchouc sunk beneath the mercury in a cistern, the caoutchouc having a groove cut in it whereby communication is ensured between the mercury in the barometer-tube and that in the cistern. The caoutchouc plate rests upon a circular sheet of thin iron, to which a handle is attached, passing above the level of the mercury in the cistern. When the level of the mercury in the barometer-tube has become constant—that is, when the whole of the liquid under examination has been converted into vapour—communication between the mercury in the barometer-tube and that in the cistern is cut off by pushing (by means of the projecting handle) the caoutchouc plate into a position such that the end of the groove is no longer covered by the barometer-tube. When the apparatus has cooled the level of the mercury is read off, and marked by means of a piece of gummed paper; the tubes are removed from their places, and the barometer-tube is filled to the mark with mercury, which is then weighed.

Hofmann has also shown, in the communication referred to, how a very small quantity of liquid may be caused to maintain the temperature of the apparatus at a constant point for an indefinite period; but it is with the first-described modification that we have here to do.

2. In the course of an investigation upon essential oil of sage, with which we are at present engaged, it became necessary for us to make several determinations of vapour-densities; these we endeavoured to perform by the use of Hofmann's modified apparatus. It occurred to us that the use of a movable caoutchouc plate was not a necessity; that, given a communication between the mercury in the cistern and that in the barometer-tube, and given a method of determining the exact height of the column of mercury in the latter at the time when the level of that liquid had become constant, it was possible, at any

time after cooling, to redetermine, and therefore to mark the spot at which the level of the mercury formerly stood. If this could be done it was of course possible to determine the capacity of that portion of the tube occupied by the hot vapour.

3. We think we have succeeded in doing away with the use of a movable caoutchouc plate, and in still retaining the great advantages of the non-graduated tube.

The barometer-tube, not necessarily of uniform bore, is supported upon a circular plate of native unvulcanised india-rubber, about 60 to 70 mm. in diameter, and 5 mm. in thickness; through this plate two holes are bored; the plate is placed upon another similar plate of cork in which two grooves are cut; each hole in the plate is immediately over the inner end of one of these grooves. A piece of glass tubing is bent so as to pass along one of the grooves in the cork, and then upwards through one of the holes in the india-rubber plate, and to project about 10 mm. above the surface of the mercury in the cistern, when the cork and india-rubber are pressed firmly upon the bottom of the cistern itself. This tube passes in the other direction over the edge of the cistern, and communicates with the condensing apparatus. A small piece of glass tubing passes through the second hole in the india-rubber plate and along the groove in the cork beneath; the upper extremity of this tube projects about 2 mm. above the surface of the caoutchouc; when the cistern is filled with mercury this tube is entirely beneath the surface of that metal. The object of the second tube is to ensure free communication between the mercury in the barometer-tube and that in the cistern; we found that the pressure of the barometer-tube upon the india-rubber plate tended to squeeze together the sides of the hole in the latter, and so to prevent free egress of mercury. When the apparatus is set up, the lower extremity of the barometer-tube must entirely cover the orifice of this tube. The outer mantle of course covers the barometer-tube and the tube communicating with the condenser. The mantle tube which we employ is of approximately uniform bore, and is not drawn out at the upper end, but is there closed by a good cork, through which passes the tube from the cistern in which the liquid—water, aniline, &c.—is boiled. In working with aniline we employ a tube of block tin as a means of communication between the cistern for liquid and the upper extremity of the mantle tube. This tin tube is unacted upon by boiling aniline, and by reason of the flexibility of the material composing it, freedom of motion is allowed while fixing the corks of the cistern and of the mantle tube firmly in their places. We generally cover the tin tube with felt or other non-conducting material.

4. When the level of the mercury in the barometer-tube has ceased to fall, we bring a pendulum cathetometer alongside of the apparatus,

adjust the pointer to the level of the mercury in the cistern, and the movable side-piece to the lower level of the meniscus in the tube; we then read off the height of the column of mercury in the barometer-tube, noting at the same time the height of the barometer and the temperature of the air. The apparatus is now allowed to cool to such a temperature as shall allow of easily grasping the outer tube. When this point is reached, the outer tube is cautiously removed, the barometer-tube being held in its place by an assistant; the latter tube is clamped securely, and by looking through the cathetometer the exact *former* level of the mercury is marked by means of a piece of gummed paper. The clamp is now removed, the barometer-tube is emptied, and dried mercury is poured in from a weighed vessel until the upper level of the meniscus is very slightly above the mark in the tube; from the result of a second weighing of the vessel the amount of mercury so poured in is determined.

5. After removing the mantle tube the small quantity of condensed aniline which has gathered on the surface of the mercury between the outer and inner tubes, flows over the mercury in the cistern, and it becomes difficult to recover the whole of it. We therefore pour mercury down a long tube from the top of the mantle, before removing the latter, until the whole of the aniline flows out through the condenser into the flask containing the main portion.

6. We do not pretend that this method enables determinations of vapour-density to be taken with anything approaching to absolute accuracy, nevertheless we think that for general purposes the method gives very fair results, and it can certainly be quickly and easily carried out. We venture to think that a fair degree of accuracy is all that is generally required in the determination of vapour-densities, and that any method for rendering the attainment of such a degree of accuracy more easy, and thence for bringing these determinations, which really give so much knowledge, into more general use, is not to be altogether despised.

7. As examples of the working of the method we subjoin the following determinations:—

H = barometer reading.

h = „ „ corrected for temperature .... = $\dfrac{H}{1+(0{\cdot}00018\times t)}$.

t = temperature of air.

v = volume of vapour in c.c. in barometer tube .... = $Hg \div \dfrac{13{\cdot}6}{1+(0{\cdot}00018\times t')}$.

Hg = weight of mercury in grams required to fill barometer-tube to mark.

t' = temperature of mercury at moment of weighing.

h' = corrected height of column of mercury in barometer-tube .. = $\dfrac{K + ts}{1 + (0{\cdot}00018 \times t^\circ)}$.

K = reading by cathetometer.

ts = tension of mercury vapour at t°.

t° = temperature of vapour (determined generally by actual experiment).

Hy = weight of volume of hydrogen equal to that of vapour, under similar conditions = $\dfrac{v \times 0{\cdot}00008936 \times 273 \times (h - h')}{760 \times (273 + t^\circ)}$.

W = weight of liquid.

Isoheptane. B. P. = 89°—91°.
C_7H_{16}.

H = 758 mm.
h = 755·6 mm.
t = 17°.
v = 75·21 c.c.
Hg = 1018·4 gram.
t' = 20°.
h' = 552 mm.
K = 562 mm.
ts = neglected as very small.
t° = 100.
Hy = 0·0013 gram.
W = 0·0628 gram.

$\frac{M}{2}$ calculated = 50.

$\frac{M}{2}$ experimental = 48·3.

Terpene from Sage Oil. B. P. = 157—160°.
$C_{10}H_{16}$.

H = 755 mm.
h = 752·7 mm.
t = 17°.
v = 73·28 c.c.
Hg = 992·15 grams.
t' = 22°.
h' = 554·5 mm.
K = 561 mm.
ts = 12 mm.
t° = 185°.
Hy = 0·00101 gram.

W = 0·0682 gram.

$$\frac{M}{2} \text{ calculated} = 68.$$

$$\frac{M}{2} \text{ experimental} = 67·5.$$

We take this opportunity of offering our best thanks to Mr. A. Barron for the aid which he has afforded us, and for the suggestions which he has made to us while carrying out the experiments, the results of which are detailed in the present note.

XIV.—*Note on the Fluid contained in a Cavity in Fluorspar.*

By J. W. MALLET, Univ. of Virginia.

THE lately revived interest in the study of liquid and gaseous substances occurring in cavities of crystallised minerals, and the hope that such study may throw light upon the conditions under which such minerals have been formed, make it desirable that observations should be extended to as many species as possible. The occurrence of cavities with enclosed liquid in *fluorspar* has been recorded, but I have seen no statements bearing on the nature of the liquid. Having a specimen of this mineral including a cavity of considerable size, with fluid contents and a readily mobile bubble, I have examined it in the same way that Mr. Hartley has of late the fluids in rock-crystal, topaz, &c., namely by careful heating.

The specimen is of green fluor, from Alston Moor, in Cumberland, consisting of a group of cubes, some of which have the edges replaced. The largest crystal is a simple cube, of 14 mm. on the side, exposing rather more than two-thirds of free surface. It contains a very irregularly shaped, flattened cavity, the greatest length of which was found to be about 6 mm., width about 2·5 mm., and depth at one place about 1 mm., lying rather to one side of the centre of the crystal. A bubble of less than 1 mm. apparent diameter shifted its place with great ease as the specimen was simply tilted in the hand. A second cavity of not more than ·6 mm. diameter, with a bubble scarcely visible without the use of a pocket lens, could be observed in another part of the crystal.

On gradually heating the whole mass, no indication whatever could be noted of the pressure of carbon dioxide. The temperature was progressively carried up to 100°, and finally to 150° C. After this last heating the principal bubble was found to have increased in size, become flattened, and in large measure to have lost its mobility, and on cooling down it appears that this condition has become permanent.

The bubble can still be moved, but requires a sharp jerk to make it change its place. This seems to be due to change in the shape and dimensions of the cavity by the pressure developed at the temperature attained. There is no easily observable increase of size of the cavity, but with low microscopic power there can be noticed an appearance of incipient splitting along a portion of its edge, and in transmitted polarised light bright coloured bands are seen surrounding the cavity, indicating compressive strains. When the bubble does move, it seems to pass through the liquid as freely as before the heating, nothing like viscidity being observable, so that the resistance to movement seems to depend merely upon change of adhesive relations to the solid sides of the cavity. From the very irregular shape of the latter I can make no satisfactory estimate of the relative volumes of its liquid and gaseous contents, save that the former must occupy by a good deal the larger space. The amount of expansion of the liquid up to the highest point of temperature was quite small.

Although it is possible that the liquid may be a hydrocarbon or an aqueous solution of hydrofluoric acid, the strong probability seems to be that it is simply water, as in so many instances has been found by Mr. Hartley (*Chem. Soc. Jour.*, March 1877, pp. 241, 242) to be true of the fluid in crystals of topaz, another fluorine mineral. The absence of carbon dioxide has some interest in connection with the supposition of that gentleman (*Chem. Soc. Jour.*, Sept. 1876, p. 248), that corundum may have been formed by the action of aluminum fluoride upon calcium carbonate. Of course topaz might conceivably be thus formed from a silicate instead of carbonate of calcium, without any liberation of carbon dioxide.

As it is stated (Greg and Lettsom, " Manual of the Mineralogy of Great Britain and Ireland," p. 23) that fluorspar crystals with cavities and enclosed fluid are not uncommon at Alston, opportunity may probably be afforded by several English collections of examining other specimens.

XV.—*On the Gases enclosed in Lignite Coal and Mineral Resin from Bovey Heathfield, Devonshire.*

By J. W. THOMAS.

THE gases present in an occluded form in the lignites of Bovey Heathfield have not, as far as I am aware, been determined, and the analyses herein noted are a continuation of the researches which I have previously had the honour of communicating to this Society, "On the Gases enclosed in various Coals" (*Chem. Soc. J.* [2], xiii, 793, and vol. xxx, 144).

The method which I employed to obtain the gases was similar to that described in a former paper (*Chem. Soc. J.* [2], xiii, 794), using, for the coal vessel, either a long tube or a Florence flask, the neck of which was hermetically joined to a bent tube for connection with the Sprengel pump.

The coals (Nos. 2 and 3) from which the gases were extracted were the best specimens now procured for fuel purposes. They were in a very moist condition, containing, as they did, from 36 to 44 per cent. of water; and in order to procure all the gas which they occlude, it is obviously necessary to use them in their wet condition.

The gases enclosed in some lignites from Bohemia were examined by Zitowitsch (*J. pr. Chem.* [2], vi, 79), who found them to consist of CO_2, O, CO, and N.

The following is a description of the coals employed:—

No. 1, lignite, consisted of the leaves and stems of plants in a closely compressed condition, and is known locally as "leafy" coal.

No. 2, lignite, was dense and compact, of a distinctly woody character, and fractured with the grain:—colour, dark brown.

No. 3, lignite, was very dense, but earthy and wet in appearance, and, to the unaided eye, structureless; the cleavage and fractures parallel with the bed much incrusted with hydrated oxide of iron colour, nearly black.

No. 4, mineral resin, is that named "Retinasphaltum," by Hatchett (*Phil. Trans.*, 1804, part I, 396). It is a brown soft powdery substance, lighter than water. All the coals yield an extract with alcohol similar to that afforded by the "resin."

A portion of No. 2 was placed in a tube and connected with the Sprengel in the usual manner. This coal contained a large proportion of water, and in consequence much of the latter became condensed in the connecting tube of the Sprengel, and was subsequently carried over by the pump into the tube used for collecting the gases. After two days' exhaustion at 100°, there was only a small quantity of gas brought over, and apparently three times as much water. The gas was analysed and its composition found to be $CO_2 = 76{\cdot}12$, $O = 0{\cdot}34$, CO 1·40 and $N = 22{\cdot}14$ per cent. In the process of analysis, the contents of the collecting tube (gas 3·2 c.c. and water over mercury) were introduced into the laboratory tube of the gas apparatus, and the gas transferred to the eudiometer; and as it was found that the water remaining in the laboratory tube continued to evolve gas, the laboratory tube and its contents were removed to another mercury trough, and the analysis of the gas above given completed with a second one. Afterwards the laboratory tube containing the water referred to was connected with the apparatus, and the water drawn over into the eudiometer, and subjected to the expanding influence of 40 inches of mercury. A further quantity of gas was given off rapidly, and 2·9 c.c. was thus obtained, which gave, on analysis, 99·83 per cent. of CO_2.

It will be seen, therefore, that the method of obtaining and collecting gases in tubes containing water is far from being trustworthy, especially when much CO_2 is present, and the collection of gas in the experiment referred to was similar in effect to the process employed by Dr. Meyer (*Chem. Soc. J.* [2], x, 798), and afterwards used by Zitowitsch, because by boiling coal with de-aërated water, much of the latter would be distilled over, and it would not be possible to collect the gases apart from it. It is probable, therefore, that the percentage of CO_2 is much too low in the results of the two lignites from Bohemia examined by Zitowitsch.

I recently determined the enclosed gas (withdrawn at 100°) in a sample of Bohemian lignite from Prenzig, near Komatau, with the following result:—$CO_2 = 96{\cdot}41$, $O = 0{\cdot}32$, $CO = 1{\cdot}20$, traces of C_nH_{2n} gases and $N = 2{\cdot}17$. The percentage of CO_2 found by Zitowitsch in the two lignites examined was 89·66 and 83·99 respectively.

Having inferred from the analysis before given of the gas obtained from No. 2, that no gas was present which would interfere with the use of strong sulphuric acid to absorb the water from the coal, I introduced a flask containing this acid between the connections of the tube containing the coal and the Sprengel pump. The gas and water evolved from the coal in a vacuum must pass through the sulphuric acid, and all the water would consequently become absorbed.

No. 2 coal was first employed, and a much larger quantity of gas was obtained than in the previous experiments without acid for dehydrating; but I could not succeed in obtaining concordant results, and, although each coal was in turn taken, and treated in the same manner, no trustworthy results could be worked out. The absorption by potash and pyrogallic acid gave very variable results, and no two analyses of the combustible portion of the gas came out alike. On account of the difficulties experienced, I undertook the experiments on gas-absorptions, the results of which were recently communicated to this Society. N_2O_2 was found to be present in the gaseous mixture, and the diminution of volume by treating with pyrogallic acid, after absorbing CO_2 by potash, was due to the absorption of N_2O_2. The N_2O_2 came from the sulphuric acid employed, and I have found from experiments that when the acid becomes diluted by the absorption of water in a vacuum, this gas is evolved in some quantity. I mention this more particularly, in case sulphuric may be employed for a like purpose, and because it is often used for dehydrating compounds in a vacuum; and in some instances probably the N_2O_2, which is evolved when the acid becomes diluted, may act upon or yield oxygen to the compound which is in process of dehydration.

After having made a number of experiments, which at first promised to give good results, they were found to be unreliable, and are not recorded in consequence.

Still retaining the globular flask in which the sulphuric acid was placed, but without any acid in it, I immersed the same in a vessel containing freezing mixture, and commenced with a portion of No. 1 coal, keeping the temperature at 50° during the first period of the experiment, in order to ascertain if any decomposition set in at 100°. It is surprising how small a quantity of water was brought over by the Sprengel, and that too when the temperature of the water cooled by the freezing mixture (ice and salt) approached that of the ordinary temperature (15°) of the laboratory. This appeared to be owing to the large internal surface of the flask, the water given off by the coal condensing on the sides; and it was found possible, by regulating the action of the Sprengel, to bring over the gas evolved at 50° almost entirely free from water without the aid of any freezing mixture. When the temperature of the lignite was raised to 100°, there was a tendency for more water to pass into the collecting tube; but by allowing the pressure of the gas (evolved in a partial vacuum) to reach about half the normal (15 inches of mercury) before working the Sprengel, sufficient gas for an analysis could be procured practically free from water. The following are the results obtained:—

No. 1, Leafy Coal (Lignite) from Bovey Heathfield.

100 grams of coal evolved 56·1 c.c. of gas at 50° after prolonged heating for 12 days and nights. During the first two days, more than 90 per cent. of the gas obtained was given off, and after the fourth day the coal appeared to be practically exhausted at 50°.

The last portion of air and gas exhausted in forming a vacuum at the ordinary temperature (13°) gave, on analyses:—CO_2 = 2·40 per cent., O = 18·66, and N = 78·94.

Analysis of the gas evolved at 50°:—

Observed pressure of gas (dry).	Temperature.	Corrected vol. at 14·5.	Progress.
498·2	14·5	498·2	Volume employed.
63·5	14·6	63·5	Vol. after absorption of CO_2.
62·4	14·9	62·31	Vol. after absorption of O.
251·3	15·0	250·84	Vol. after adding O.
481·4	15·0	480·52	Vol. after adding H.
126·0	14·5	126·0	Vol. after explosion.
107·8	14·6	107·76	Vol. after absorption of CO_2.
411·5	14·4	411·65	Vol. after adding H.
221·6	14·4	221·68	Vol. after explosion.

Composition in 100 parts.

CO_2 .... =	87·25
O .... =	·24
CO............ =	3·59
N .... =	8·92
	100·00

No. 1, lignite, after heating at 50°, was kept at 100° for 18 days and nights, the loss of water (in a beaker kept boiling around coal) by evaporation being renewed by a self-acting contrivance similar to Bishof's apparatus for water analysis. The gas came over rapidly for the first hour, but only traces were afterwards obtained.

100 grams of coal evolved 59·9 c.c. of gas at 100°. A rather considerable portion of water and oily matters having a somewhat agreeable aromatic odour was brought over by the Sprengel, owing to the length of time which the coal was maintained at 100°. The composition of the gas, after correction for the amount of gas extracted from the water in the collecting tube by placing it under diminished pressure, was found to be:—

CO_2 .... =	89·53
C_nH_{2n} gases =	·33
CO .... =	5·11
N .... =	5·03
	100·00

The beaker containing boiling water in which the tube holding the coal was immersed was removed, and a paraffin bath substituted for it.

The temperature was then raised and maintained at 200°. At about 150° decomposition set in, and the surface of the mercury in the collecting tube, as also the pellets of the metal as they fell down the Sprengel capillary tube, became blackened by the formation of sulphide of mercury. The contents of the first tube collected emitted a very powerful, but somewhat agreeable, aromatic odour; while the sulphide of mercury adhered in scaly films to the inside of the collecting tube. The second tube of gas brought over presented the same appearance as the first as regards the deposit of sulphide, but a most disagreeable odour marked the presence of the aromatic compounds. The third tube was coated with sulphide of mercury, but emitted a still more disagreeable odour than the second—the odour of organo-sulphur compounds, among which mercaptan appeared to be present. After the gas was transferred to the apparatus for analysis, the odour of the more volatile sulphur-compounds gradually disappeared, leaving an unmistakable evidence of the presence of sulphide of allyl. Some of the latter compound was made from garlic, for the purpose of comparison. During the time the analysis and collection of the gas evolved at 200° was proceeding, my laboratory was for days scented with the fragrance of garlic and onions. Great difficulty was experienced in removing the oily and empyreumatic vapours from the Sprengel and connecting tubes, as well as from the endiometer of the gas apparatus. The gas retained the vapour of allyl-sulphide, after absorbing C_nH_{2n} gas by fuming sulphuric acid. The quantity of gas evolved at 200° during the first hour was very considerable, but soon became very much less.

Composition of first 18 *c.c. evolved at* 200°.

Observed pressure of gas (dry).	Temperature.	Progress.
305·7	12·8	Volume employed.
35·5	12·8	Vol. after absorption of CO_2.
126·5	12·8	Vol. after adding H.*
119·4	13·0	Vol. after absorbing with fuming sulphuric acid.
92·4	13·0	Vol. after absorbing CO by ammonio cuprous chloride.

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* Hydrogen was added to increase the volume of gas, in order to absorb C_nH_{2n} gases.

Composition of gas in 100 parts.
CO_2 .... = 88·39[*]
C_nH_{2n} gases .... = 2·32
CO .... = 8·83
N and undetermined gas = ·46

100·00

A second analysis of the first portion of gas collected showed by indirect estimation, that the gas absorbed by fuming sulphuric acid was one of low carbon atoms, probably C_2H_4. The second tube of gas evolved at 200° was analysed with the following result:—

Observed pressure of gas (dry).	Temperature.	Corrected vol. at 16·2°.	Progress.
535·4	16·1	535·5	Volume employed.
520·1	16·2	520·1	Vol. after absorbing SH_2 (MnO_2).
80·9	16·2	80·9	Vol. after absorbing CO_2.
[†]162·3	16·2	162·3	Vol. after absorbing CO_2 (total gas).
12·0	16·2	12·0	Vol. after absorbing CO by ammonio cuprous chloride.
232·7	16·3	232·62	Vol. after adding O.
394·1	16·3	393·96	Vol. after adding H.
128·6	16·4	128·51	Vol. after explosion.
102·5	16·4	102·43	Vol. after absorbing CO_2.
429·3	16·5	428·83	Vol. after adding H.
126·3	16·5	126·16	Vol. after explosion.

Composition in 100 parts.
CO_2 .... = 82·06
SH_2 .... = 2·82
CO.......... = 14·00
C_2H_4 .... = ·49
C_3H_6 .... = ·48
N .... = ·15

100·00

In the above analysis the calculating volumes are of course too close to theory to be correct, as there is doubtless some vapour of the sulphur-compounds and oily matters present as well.

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[*] There is a small percentage of SH_2 included in the CO_2 left undetermined by mistake.

[†] This vol. is the total gas contained in the second tube, less SH_2 and CO_2; the preceding vol. represents about one-half of the total gas.

An analysis of the last gas collected at 200° showed that the percentage of CO_2 was gradually decreasing, while the CO increased. The same portion of coal No. 1 was heated up to 250° with the intention of raising the temperature to 300°, but this was prevented, owing to the action of the sulphur-compounds upon the mercury being so energetic, that the capillary tube of the Sprengel became blocked up. Acid vapours of similar odour to those evolved during the carbonisation of wood in iron retorts were given off towards the end of the experiment. A portion of gas collected at 250° was analysed, with the following results:—

	Composition in 100 parts.
SH_2 .... =	5·85
CO_2 .... =	71·13
C_nH_{2n}.......... =	1·09
CO .... =	16·20
CH_4 .... =	5·46
N .... =	·27
	100·00

No. 2, Lignite (woody) from Bovey Heathfield.

100 grams of lignite evolved 48·5 c.c. of gas at 50°.

An analysis of the last portion of air exhausted in forming a vacuum gave CO_2 = 4·52 per cent., O = 14·52, traces of CO and N = 80·96. This portion of air and gas measured 15·1 c.c. A small portion of air collected previous to this gave 20·79 per cent. of O. The quantity of coal employed in this experiment was very large, viz., 140·3 grams. It is a remarkable fact that nitrogen escapes from coal more rapidly than apparently any other gas. This circumstance may be noticed in the analyses of the enclosed gases given in the previous papers. The gas evolved at 50° was collected in five separate tubes, and the gaseous contents of each was subjected to analysis.

Analyses of the Gas evolved at 50°.

	1st portion.	2nd portion.	3rd portion.	4th portion.	5th portion.
Carbonic anhydride	79·12	96·62	97·29	96·10	96·23
Oxygen..........	·51	·33	·21	·19	·11
Carbonic oxide....	4·14	lost	1·40	2·93	2·42
C_nH_{2n} gases	trace	,,	trace	trace	trace
Nitrogen	16·23	,,	1·10	0·78	1·24
	100·00		100·00	100·00	100·00

The average percentage of CO_2, after allowing for the difference in volume of the gas in five tubes, was about 94 per cent. Some oily matters, having a pleasant aromatic odour, were brought over by the pump. These aromatic compounds must have low boiling points, as they are evolved at 15° in a vacuum. After remaining night and day in a vacuum at 50° for eight days (No. 2, woody), the temperature was raised to 100° and maintained for 14 days and nights.

100 grams of lignite evolved 114·3 c.c. of gas at 100°.

Analyses of the Gas evolved at 100° (1*st portion*).

Observed pressure of gas (dry).	Temperature.	Progress.
521·6	12·2	Volume employed.
17·0	12·2	Vol. after absorbing CO_2.
2·4	12·3	Vol. after absorbing CO.

		Composition in 100 parts.
CO_2	=	96·74
CO	=	2·80
N and other undetermined gas	=	·46
		100·00

The second, third, and fourth portions of gas evolved at 100° were mixed, and the CO_2 determined in a small part, and found to be 96·05 per cent. The CO_2 was then absorbed from the whole of the gas, and the residue used for determining the carbon gases. The composition in 100 parts was—

CO_2	=	96·05
CO	=	3·20
C_nH_{2n} gases	=	·33
N	=	·42
		100·00

The contents of five other tubes were treated in a similar manner, the composition of the mixed gas for 100 parts being—

CO_2	=	95·34
CO	=	3·83
C_nH_{2n}	=	·61
N	=	·22
		100·00

The calculated volumes of the combustible gas showed the presence of traces of higher hydrocarbons.

Had the coal remained longer in a vacuum at 100°, a little more gas would be evolved, but the quantity was gradually growing less and less. Small yellow crystals of sulphur, which I mistook at first for succinic acid, were formed by sublimation from the coal, on the inside of the tube, just above the level of the boiling water in which the tube was immersed, and this happened in every instance in which this lignite (No. 2, woody) was employed, but not so with the other lignites.

A fresh portion of No. 2 lignite was heated up to 200°, after previous heating for some time at 100°. When the temperature rose to 180° there was no apparent change, the pump bringing over only traces of gas. At 185° destructive distillation commenced. The tube in which the gas evolved at 200° was collected emitted the odour of sulphide of allyl, but only traces of SH_2 were present in the gas collected, as there was much moisture in the Sprengel connections. The quantity of sulphur compounds evolved by No. 2 lignite at 100° was not so great as that given off by the other coals. The aromatic odour of the oily matters, which belong probably to the terpenes, was distinguishable, although masked in a great degree by the allyl sulphide.

Analysis of the Gas evolved at 200°.

Carbonic anhydride	86·30
Carbonic oxide	7·41
Gases of the C_nH_{2n} series	2·08
Marsh gas	3·34
Hydride of propyl	·53
Nitrogen	·34
	100·00

The above figures were obtained from closely agreeing analyses. The calculating volumes indicated that C_3H_8 was present, and the result is made out accordingly. It is possible, however, that the vapour of liquid compounds may take part in the explosion, although the greater portion would be broken up by the fuming sulphuric acid used for absorbing the C_nH_{2n} gases.

No. 3, Lignite, from Bovey Heathfield.

This coal was heated *in vacuo* at 50° for four days and five nights, when gas was evolved equal to 68·1 c.c. per 100 grams of lignite. The last portion of air and gas exhausted in forming a vacuum at the ordinary temperature gave CO_2 = 2·42 per cent., O = 17·26, and N = 80·32. The gas evolved at 50° was collected in three tubes.

Analysis of the Gas collected at 50° (2nd tube).

Observed pressure of gas (dry).	Temperature.	Corrected vol. at 12°.	Progress.
377·1	11·8	377·37	Volume employed.
6·4	11·8	6·4	Vol. after absorbing CO_2 (portion of gas).
11·9	12·0	11·9	Vol. after absorbing CO_2 from whole of gas.
11·7	12·0	11·7	Vol. after absorbing O.
163·2	12·0	163·2	Vol. after adding O.
289·9	12·1	289·8	Vol. after adding H.
94·4	12·2	94·33	Vol. after explosion.
84·3	12·4	84·18	Vol. after absorbing CO_2.
349·9	12·6	349·13	Vol. after adding H.
103·6	12·6	103·38	Vol. after explosion.

	Composition in 100 parts.
Carbonic anhydride	98·30
Carbonic oxide	1·35
Hydrocarbon gas	trace
Nitrogen and trace of O	0·35
	100·00

The gas in first and third tubes was analysed with the following result:—

Composition of gas in	1st tube.	3rd tube.
Carbonic anhydride	94·12	98·27
Oxygen	·28	—
Carbonic oxide	2·13	1·15
C_nH_{2n} gases	trace	·19
Nitrogen	3·47	·39
	100·00	100·00

The average percentage of carbonic anhydride was 96·83.

The same portion of coal (No. 3) was next heated to 100° during two and a half days and two nights, when gas was evolved equal to 86·3 c.c. per 100 grams of lignite.

The following is the composition of the gas evolved at 100°, 66 c.c. being used for the determination of the combustible gas.

Observed pressure of gas (dry).	Temperature.	Corrected vol. at 16·2°.	Progress.
332·6	16·2	332·6	Volume employed.
7·4	16·2	7·4	Vol. after absorbing CO_2.
7·4	16·6	7·4	Vol. after absorbing O.
43·7	16·8	43·6	Vol. after absorbing CO_2 and O from 66 c.c. of gas.
39·8	16·6	39·74	Vol. after absorbing with fuming sulphuric acid.
149·2	16·4	149·10	Vol. after adding O.
206·0	16·3	205·93	Vol. after adding H.
103·6	16·3	103·56	Vol. after explosion.
69·8	16·2	69·8	Vol. after absorbing CO_2.
286·1	16·2	286·1	Vol. after adding H.
95·9	16·2	95·9	Vol. after explosion.

	Composition in 100 parts.
Carbonic anhydride	97·77
Carbonic oxide	1·69
C_nH_{2n} gas	·21
Nitrogen	·33
	100·00

The same portion of coal (No. 3) was next heated to 200°, when a considerable quantity of gas was evolved, active decomposition having commenced about 180°.

Analysis of the Gas evolved at 200.°

	Composition in 100 parts.
Sulphuretted hydrogen	0·41
Carbonic anhydride	91·68
C_nH_{2n} gases	·41
Carbonic oxide	7·12
Hydrogen	traces
Nitrogen	·38
	100·00

No 4, Mineral Resin, from Bovey Heathfield.

This substance was heated at 50°, but did not yield sufficient gas for analysis. The temperature was raised to 100° when gas was evolved equal to 21·4 c.c. per 100 grams of substance.

The last portion of air and gas exhausted in forming a vacuum at the ordinary temperature (15°) gave on analysis $CO_2 = 2·65$, $O = 17·94$, $N = 79·41$.

Analysis of the Gas evolved in vacuo at 100°.

Observed pressure of gas (dry).	Temperature.	Corrected vol. at 11·8°.	Progress.
256·0	11·8	256·0	Volume employed.
30·1	11·7	30·1	Vol. after absorbing CO_2.
29·5	11·8	29·5	Vol. after absorbing O.
28·3	12·0	28·3	Vol. after absorbing C_nH_{2n} gases by fuming sulphuric acid.
183·0	11·9	182·94	Vol. after adding O.
274·7	12·0	274·50	Vol. after adding H.
126·7	11·8	126·7	Vol. after explosion.
104·1	11·8	104·1	Vol. after absorbing CO_2.
375·5	11·8	375·5	Vol. after adding H.
87·5	11·8	87·5	Vol. after explosion.

	Composition in 100 parts.
Carbonic anhydride	88·24
Oxygen	·23
C_nH_{2n} gases	·47
Carbonic oxide	7·90
Nitrogen	3·16
	100·00

The tube containing the mineral resin was further heated in a paraffin-bath with the intention of raising the temperature to 200°. Between 110° and 120° the "resin" began to melt, and decomposition set in at once. Much sulphur compounds were evolved, which attacked the mercury in the pump to such an extent, that before the "resin" was heated above 160° it became impossible to bring the gas over. Previous to this, however, a quantity of gas was obtained equal to 180 c.c. per 100 grams of substance. The odour of the vapour present in the tube in which the gas was collected, was not unlike that of the so-called oil of amber—no sulphide of allyl was present. The composition of the gas obtained at 150°, calculated from closely agreeing figures, was—

	In 100 parts.
Sulphuretted hydrogen......	0·41
Carbonic anhydride	78·88
C_nH_{2n} gases	2·67
Carbonic oxide	7·82
Marsh-gas	8·05
Hydride of propyl..........	1·86
Nitrogen..................	·31
	100·00

When the Bovey Heathfield lignites are compared with the coals of the carboniferous period, there exists as much difference with regard to their occluded gas as there is to their structure and general character. The chemical composition of the lignites approach that of some of the cannel and bituminous coals, but their structure is very dissimilar. So far as the occluded gas is concerned, these lignites approach nearer to the cannel coals than any other, but there are material differences between them. The greater portion of the gas enclosed in cannel coal and lignite consists of CO_2, but, while the former contains the gases, and apparently the compounds of the paraffin series, the latter contain C_nH_{2n} gases, and oily matters of the aromatic series, in addition to appreciable quantities of CO.

The lignites are far less stable bodies than the coals of the carboniferous formation, as they undergo decomposition *in vacuo* at a much lower temperature—all those examined below 200°. The coals of the carboniferous period remain unaltered at that temperature, and usually resist decomposition at 300°.

It is possible that slow oxidation, proceeding at the expense of the combined oxygen, may take place *in vacuo* at 100°, but, as will be seen from the analyses, there is no difference in the nature of the gases evolved either at 50° or 100°.

The apparent traces of C_nH_{2n} and other gases which are calculated and recorded in percentage in some of the analyses, would lead one, at first sight, to ridicule the idea of attempting such calculation; but by absorbing the CO_2 from a *large* volume of gas, 50 c.c. for instance, a very appreciable residue could be obtained for the purpose of determining the C_nH_{2n} gases, CO, &c.

With regard to the sulphur compounds, and to the state of combination in which the sulphur exists in the lignites, very little absolute information has been obtained. The crystals of sublimed sulphur deposited from No. 2 at the temperature of 100° *in vacuo*, seem to show that some sulphur compound is present, which is capable of being decomposed with facility, or that free sulphur exists in the lignite. When there was little water in the Sprengel connections, a considerable quantity of SH_2 was mixed with the gas collected, but the reverse was the case when much moisture was present. Owing to the fact that the figures of the analyses did not show the presence of free hydrogen (excepting the one instance where there appeared to be a trace), it is very probable that the sulphur of the mercury sulphide formed in the Sprengel and collecting tube was derived from the breaking up of some sulphur-compound other than SH_2. When the gas was imprisoned between the pellets of mercury (as the Sprengel was in the act of bringing over the gas) an energetic action appeared to be going on, as shown by the very appreciable quantity of sulphide of mercury formed. It is probable, therefore, that the nature of some of the sulphur compounds evolved in a vacuum by the coal, were altered or broken up before reaching the collecting tube, the more stable, especially sulphide of allyl, alone escaping decomposition. The presence of sulphur in organic combination in No. 1 and No. 3, which contain, in their fresh condition, hydrated oxide of iron between the natural cleavages of the coal, as also in some parts throughout their mass, indicates that the process of conversion of these substances into true coal has not advanced sufficiently to convert the organo-sulphur compounds into sulphide of iron. The films of oxide of iron referred to, which are deposited probably by the reducing action of the coal upon iron salts dissolved in the water which sinks into the coal strata, suggest that the layers of iron pyrites, and crystalline nodules of the same may have derived their sulphur from that which originally existed in organic combination in the plants from which coal is produced. This view is more in harmony with the fact of organo-sulphur compounds being present in the coal while hydrated oxide of iron is deposited on its mass, because, it is evident that if we regard the iron pyrites of coal as the product of the reduction of sulphates by organic matter, the sulphur so liberated would enter into combination with the iron oxide in preference to forming organo-sulphur compounds. In those instances in which sulphur has been found in coal in the state of organic combination, its detection has resulted from the finding of more sulphur than corresponded with the amount of iron in the ash of the coal.

Had a portion of coal No. 1 or No. 3 been subjected to analysis, the sulphur it contains would not be regarded as being in organic combination owing to the ample quantity of ash present. The sulphur and ash in these coals calculated on the dry sample were determined wit the following result:—

	No. 1.	No. 3.
Sulphur	1·53	1·71
Ash	36·07*	17·98

* Containing SiO_2, 25·11.

The hygroscopic character of lignite has been pointed out by several observers. The Bovey lignites are especially hygroscopic, and so great is the affinity of these substances for waters, that they will reabsorb from 10 to 12 per cent. in the space of a few hours after being thoroughly desiccated. All the water is not driven off from the lignites which I examined at 50°, even in a vacuum, and after the coal has been completely desiccated at 100° in a vacuum, and the temperature allowed to fall to 30°, the aqueous vapour, which pervades the vacuous space, is absorbed by the dry lignite, so rapidly, that the condensed water in the Sprengel tubes and connections flashes into vapour to supply its place until in a short time the whole of the water is reabsorbed, providing it does not exceed 10 per cent. of the coal by weight.

In conclusion, I would express my grateful thanks to Wentworth Buller, Esq., for his kindness in supplying the samples of lignite and mineral resin.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Electric Resistance of Liquids under High Pressures. By H. HERWIG (*Pogg. Ann.*, clx, 110—113).—A pressure of eighteen atmospheres was found to effect no change in the electric resistances of several very dilute saline solutions, the resistances remaining practically the same as under the ordinary atmospheric pressure.

R. R.

Penetration of Platinum by Electrolytic Gases. By H. HELMHOLTZ and E. ROOT (*Chem. Centr.*, 1876, 401).—The authors having been led by previous experiments to anticipate that hydrogen produced by electrolysis upon one side of a thin platinum plate would after some time make itself perceptible on the opposite side, and so bring about galvanic polarisation, undertook experiments the results of which prove their anticipations to have been correct.

F. J. L.

Mechanical Actions of Incandescent Gases. By A. DAUBRÉE (*Compt. rend.*, lxxxiv, 413—419).—A plate of steel having a surface of 23 square centimeters and weighing 3·479 grams was placed in a closed powder-chamber of 43 cubic centimeters' capacity in which 12 grams of powder were exploded by an electric spark. The plate of steel was found completely fused into a strangely twisted and puffed-out mass. In the chamber was found, besides the ordinary products of the combustion of gunpowder, an impalpable powder of sulphide of iron, and the weight of the steel was found to be reduced to 2·741 grams. Similar experiments with smaller charges of powder exhibited modified effects. The signs of fusion were visible only on the edges of the plate, but the metal had completely changed its physical characters, having become white like silver and extremely brittle. It had lost only one-sixth or one-seventh of its weight, and the pulverulent sulphide was found as before.

In another series of experiments, the chamber in which the powder was ignited, communicated by an extremely small opening with a cylindrical passage in the wall of the powder-chamber. This cylindrical passage terminated interiorly in a cone, at the apex of which was the small opening into the powder-chamber. Into the passage a cylindrical steel plug was fitted, which would, had it been completely screwed up in its seat, have entirely closed the communication between the interior of the powder-chamber and the external air. But in the experiments the conical termination of the plug was not forced into perfect contact with the conical termination of the passage, and this permitted an extremely narrow channel, through which, at the moment of explosion, the incandescent gases could rush out. Though the discharge lasted but the fraction of a second, the terminal cone of the steel plug had completely disappeared, and the cylindrical part had deep furrows excavated from its substance. The incandescent gases, impelled by a pressure of 1,500 atmospheres, had melted the steel and carried it out, as the presence in the apartment of an impalpable black magnetic powder proved. When the plug was in its place and the explosion was produced without allowing the gases to escape, no alteration whatever took place in its form.

The author alludes to the bearing of these observations upon some of the problems which geologists and mineralogists are called upon to solve. He refers to the high pressures which are known to exist in subterranean reservoirs, as in that from which lava is forced up to the summit of Etna, more than 3,000 meters above the sea-level. The pressure required for this is comparable with that in the powder-chamber employed in his experiments, and water under such a pressure escaping through narrow fissures may carry up substances in a state of sub-division so minute as to appear the result of sublimation.

R. R.

A New Method of observing Melting Points. By HIMLY (*Pogg. Ann.*, clx, 102—110).—The bulb and part of the stem of a glass mercurial thermometer are chemically coated with a film of silver, and a copper wire is attached to the coated part, a little above the bulb, by twisting the wire round the stem. This wire passes along the stem and is secured above by an india-rubber ring. A thin layer of copper is then deposited electrolytically over the silvered part of the instrument, the wire serving for this purpose, and remaining as part of the arrangement for subsequent use. To determine the melting point of any easily-fusible non-conductor of electricity, the coated thermometer is dipped for an instant into the melted substance, and when it has become cold and the substance has resumed the solid form, it is placed in mercury contained in a porcelain vessel. This mercury and the metal covering the bulb of the thermometer are placed in connection with the respective poles of a galvanic element, so that the passage of the current is prevented only by the thin layer of non-conducting substance. When the mercury is very slowly heated by means of a glycerin bath or other convenient arrangement, the circuit will be closed the instant that liquefaction of the non-conducting layer occurs, and passage of the current being announced by an electric bell included in the circuit, the reading of the thermometer at that instant indicates the melting point. By proper modifications of the arrangements, the author makes the same principle applicable to the determination of melting-points of conductors of electricity.

R. R.

Elasticity of Metals at different Temperatures. By G. PISATI (*Gazzetta chimica italiana*, vii, 61—89).—This is a continuation of the author's researches on the elasticity of metals as measured by torsion (this Journal, 1877, i, 38). In this portion of the memoir the author gives in detail the results he has obtained with wires of iron and steel both annealed, of copper and brass, both hard and annealed, of hard gold and aluminium, and with platinum both hard and annealed. From the numbers obtained it would appear that the hard metals have generally a higher modulus of torsion than the corresponding metals when annealed, but that for each metal the difference between the moduli decreases with elevation of temperature, and that in such a manner that the curves of the moduli would ultimately intersect: this actually happens in the case of copper at 250°. The total number of oscillations is usually greater for the annealed metals, although the contrary is the case with brass from the ordinary temperature to 165°, and for platinum above 220°, but in order to compare rigorously the influence of annealing on the various metals as affecting the total number of oscillations occurring at various temperatures, it would be necessary to make experiments with perfectly similar wires of hardened and annealed metals under precisely identical conditions.

It is noteworthy that after the second series of experiments made with the annealed brass wire in the manner employed by the author and previously described, the total number of oscillations, instead of increasing or remaining constant, diminished rapidly until they were nearly the same as those of the first series, a corresponding change occurring in the mean duration of the oscillation. It would seem also that at no temperature does aluminium rigorously fulfil the law of Weber and Gauss, the experimental numbers differing considerably from the calculated ones. C. E. G.

The Torricellian Vacuum. By J. MOSER (*Pogg. Ann.*, clx, 138—143).—The paper describes a series of experiments with barometer tubes of a peculiar construction, and the author's conclusion from his results is that some air is always present in the so-called vacuum of Torricelli. R. R.

Inorganic Chemistry.

Iodine Trichloride. By A. C. CHRISTOMANOS (*Deut. Chem. Ges. Ber.*, x, 434—441).—To obtain this substance in the pure state and free from iodine, the author avails himself of the action of chlorine on hydrogen iodide—

$$HI + 2Cl_2 = HCl + ICl_3.$$

Pure hydrogen iodide, obtained by adding iodine gradually to a mixture of amorphous phosphorus with a few drops of water gently heated in a retort, is passed through a calcium chloride drying-tube into a tall cylinder or flask filled with dry chlorine. At the first contact of the two gases a dense white cloud of hydrogen chloride is formed, in which float innumerable golden-yellow spangles of iodine trichloride. When the hydrogen iodide is in excess, the fumes have a reddish-violet colour, and the spangles of trichloride then assume a still more brilliant appearance. Generally, if the two gases are tolerably pure, the hydrogen iodide takes fire in the chlorine. Violet fumes of iodine are then set free, which immediately combine with chlorine to form brilliant golden-yellow crystals of trichloride, whilst the hydrogen burns with a bright red flame in iodine-vapour. The sides of the cylinder speedily become covered with yellow crystalline scales of the trichloride. If after this the current of hydrogen iodide be continued, the crystals assume a darker colour, becoming orange and brown, and finally deliquescing, owing to the following reaction:—

$$HI + ICl_3 = HCl + 2ICl.$$

The process forms a very striking lecture experiment.

Iodine trichloride is a lemon- to orange-yellow solid, very easily decomposible. It can be preserved only in an atmosphere of chlorine. In the air it volatilises perceptibly, even at − 12°. It is less volatile in carbon dioxide, especially when cooled to − 12°, but it still loses weight distinctly, and at the same time an odour of carbonyl chloride, $COCl_2$, is perceptible. When heated to 100° in an open glass tube it is instantly decomposed into free chlorine and iodine monochloride, which latter boils rapidly at that temperature. In an atmosphere of chlorine the trichloride melts at 33°. It dissolves in water. Strong sulphuric acid throws down from the concentrated aqueous solution a yellow powder; but the same acid dissolves the trichloride with yellow colour. The trichloride dissolves in potash, forming iodide, chloride, iodate, and chlorate. In an atmosphere containing ammonia it emits dense white fumes. An excess of ammonia immediately converts it into nitrogen iodide, sal-ammoniac, and ammonium iodide. The trichloride dissolves in benzene with dark cherry-red colour. It is immediately decomposed by carbon bisulphide, sulphur chloride being formed. It oxidises solutions of sulphur dioxide and ferrous sulphate when boiled therewith. Potassium and phosphorus take fire in contact with it. The trichloride volatilises in a current of hydrogen in the cold without acting upon it; but on gentle heating hydrogen chloride and liquid iodine monochloride are formed. J. R.

On Sulphuric Anhydride and a New Sulphuric Hydrate. By R. Weber (*Pogg. Ann.*, clix, 313—327).—This paper commences with a review of former experiments on the preparation of sulphuric anhydride, which the author thinks have been rendered inaccurate to a certain extent by the presence of small quantities of the hydrate. He describes his plan for the preparation of the pure anhydride, which is rendered difficult from the ready manner in which access of moisture takes place during the distillation of the anhydride, unless conducted in hermetically sealed vessels. The method adopted is to distil carefully fuming oil of vitriol, condensing the impure anhydride formed in a receiver cooled to 12—15°. This being partially purified by fractional redistillation, a liquid is obtained more fluid and purer than the first product, and like it solidifying quickly. This substance is again purified by distillation in a bent and hermetically sealed tube of from 6 to 8 mm. diameter, the limb of which is not shorter than 20 cm. By this means the passage of fluid particles is prevented, and a cohobation rendered possible. At the end of one of the limbs by the narrowing of the tube a vessel about 30 mm. long is formed, in which the particles of hydrate produced in the first distillation collect. Further purification is effected by redistillation in a manner fully described in the memoir. The pure anhydride prepared by the author is at moderate temperatures a very mobile colourless liquid, which solidifies on slow cooling to long transparent prismatic crystals like saltpetre, quite different from the white opaque needles of the ordinary anhydride. The crystals melt at 14·8° C. Under certain circumstances the anhydride can, like sulphuric hydrate, be cooled to temperatures below its liquefying point without solidification, but then becomes suddenly solid.

The anhydride shows the same composition after the lapse of a year, and retains the same melting point as that freshly prepared. The author cannot, therefore, agree with the view sometimes taken, that isomeric modifications of the anhydride exist, nor does he agree with the views of Marignac and Schultze-Sellac on the changes which the anhydride is supposed to undergo by time. By the addition of a little moisture to the pure anhydride a solid substance is formed, consisting of flakes when in small quantities. With a greater amount of water a more cohesive body is obtained, which, combining with a part of the anhydride, forms a jelly-like substance. The body obtained is perfectly white and opaque, and passes into vapour without liquefying. It has not as yet been obtained sufficiently pure or in sufficient quantities to allow of its composition being studied. Besides this body, containing the minimum quantity of water, the author mentions the existence of another intermediate product formed by the gradual addition of English oil of vitriol to the ordinary anhydride. Care is necessary in the addition of the oil of vitriol, as too small quantities hinder the deposition of the crystals formed in the cooling of the fluid, whilst too large a quantity promotes the formation of Mitscherlich's solid hydrate, $H_2SO_4.SO_3$. The body in question is at ordinary temperatures a viscous liquid, solidifying from 8—10°, and possesses a density of 1·983. The analysis of the body leads to the following formula, $H_2SO_4.3SO_3$, or $H_2S_4O_{13}$, which requires a percentage of 94·69 SO_3. J. M. T.

Decomposition of Glass. By V. DE LUYNES (*Compt. rend.*, 303—305).—Various pieces of old glass were found to be covered with scales containing nearly 80 per cent. of silica, while the glass itself never contained more than 68 per cent. This change of condition does not diminish the transparency of the glass.

F. D. B.

Glass impervious to Gases. By G. QUINCKE (*Pogg. Ann.*, clx., 118—123).—The author's experiments prove that glass 1·5 mm. in thickness is capable of retaining for 17 years, without sensible loss, hydrogen gas having a tension of 100—126 atmospheres. The same result was obtained with carbonic acid gas under somewhat lower pressures. R. R.

Decomposition of Crystallised Potash-alum at 100°. By Alex. Naumann (*Deut. Chem. Ges. Ber.*, x, 456—459).—The author finds that crystallised potash-alum gradually undergoes dissociation when heated to 100° in sealed tubes. The fused substance first gives off water of crystallisation, and deposits a solid compound (probably anhydrous alum), after which there is formed in the liquid a basic compound of alumina, potash, sulphuric acid, and water, corresponding with that formed in alum solutions heated to 100°, as formerly described by the author.

In one experiment 15 grams of freshly crystallised air-dried alum was sealed up in a glass tube and placed in boiling water, when the alum melted to a perfectly clear liquid. In three hours a distinct turbidity appeared, and in five hours the liquid became quite opaque from separation of an apparently amorphous solid, which at the end of four days had settled down, leaving the supernatant liquid clear. At the same time crystalline laminæ were formed on the sides of the tube.

The deposited solid (weighing 8·5 grams) when treated with cold water, left 6 per cent. of insoluble residue (basic compound). The soluble portion was found to contain sulphuric acid, alumina, and potash in the same proportions as crystallised alum, as was also the case with the liquid contents of the tube. J. R.

Researches upon the Metals of the Tantalum-group, and upon Neptunium, a new Metal. By R. Hermann (*J. pr. Chem.* [2], xv, 105—150).—The supposed new metal was discovered in a mineral (sent to the author) and called tantalite, from Haddam, Connecticut, U.S. The mineral proved to be a mixture of nearly equal parts of columbite and ferroilmenite. The author believes that this mineral contains the metal *ilmenium*,* previously supposed to have been discovered by him, in addition to *neptunium*, niobium, and tantalum. His analysis of the specimen is—

Ta_2O_5.	Nb_4O_7.	Il_4O_7.	Np_4O_7.	
32·39	36·79	24·52	6·30	= 100

The mineral was fused with potassium hydrogen sulphate; the mixture of metallic hydrates so produced was successively digested with ammonium sulphide and hydrochloric acid; the moist mass was dissolved in hydrofluoric acid, an equivalent quantity of potassium-fluoride was added, and the whole was diluted, so that 40 parts of water were present to each part of fluoride. The double potassio-tantalic fluoride separated out on cooling. By evaporating the filtrate and crystallising, mixtures of potassio-niobic, and potassio-ilmenic fluorides were obtained, while potassio-neptunic fluoride remained in solution, together with small quantities of the double niobium salt. The filtrate was diluted and heated to boiling. Soda was then added, whereby a precipitate of sodium neptunate containing sodium niobate was thrown down. This precipitate was collected, pressed, and boiled with 25 parts of water: the niobate was then dissolved. The residual sodium neptunate was fused with potassium-hydrogen sulphate, the fused mass was washed with water until free from acid, and dried over sulphuric acid. The hydrate thus obtained is not soluble in weak mineral acids, with the exception of hydrofluoric. The solution in the latter acid is not precipitated by sulphuretted hydrogen. The hydrate is not acted upon by ammonium sulphide. Dilute boiling solutions of neptunium fluoride yield amorphous precipitates with caustic soda: the precipitates are insoluble in boiling water: in this respect the new metal differs from niobium and ilmenium. Neptunium is distinguished from tantalum by the fact that its fluoride forms an easily soluble double salt with potassium fluoride.

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* In the *J. pr Chem.*, xxxviii, 91—119; xl, 475; and xlv, 52, appeared Hermann's papers, in which he stated his reasons for believing that Siberian ytthrotantalite contained an oxide of a new metal, *Ilmenium*. Rose, in *Pogg. Ann.*, lxxi, 157, showed that this ilmenium oxide was probably only impure niobium oxide, and that the yttroilmenite of Hermann was really samarskite, containing a little tungstic acid.—M. M. P. M.

Neptunium oxide, or sodium neptunate, colours the microcosmic salt bead yellow in the inner flame. Ilmenium salts give a brown colour to the same bead.

Tincture of galls, followed by addition of hydrochloric acid, forms a brick-red precipitate with ilmenates, and a cinnamon-brown precipitate with neptunates. The hydrated oxides of neptunium, ilmenium, and niobium are dissolved by a large excess of concentrated hydrochloric acid in presence of tin-foil, forming intensely blue liquids. The hydrated oxide of tantalum is neither dissolved nor coloured under the same conditions.

From an analysis of the double fluoride of neptunium and potassium, and on the assumption that 2 atoms of potassium are present for 1 atom of neptunium, the number 118 is deduced as the atomic weight of the latter metal.

Hydrates of the general form Me_4O_7, prepared by fusing the various oxides of neptunium, ilmenium, and niobium with potassium-hydrogen sulphate, washing with water until all acid was removed, and drying over sulphuric acid, are described. The hydrate of neptunium has the composition $Np_4O_715H_2O$; it is a white powder resembling magnesia: when heated it loses 31·5 per cent. of its weight; during the process of heating the substance appears to glow. The specific gravity of the dehydrated residue, Np_4O_7, is 4·51. On the assumption that this formula really represents the composition of the oxide produced by heating the hydrate described, and that the true atomic weight of neptunium is 118, the author deduces the number 18 as representing the atomic volume, and hence the number 6·5 as representing the specific gravity of neptunium. The metals tantalum, neptunium, ilmenium, and niobium may be separated by the process employed by the author for the analysis of the mineral from Haddam, and described at the beginning of this abstract. Niobium and ilmenium may be separated by fractional precipitation of the double potassium fluorides, or of sodium niobate and ilmenate.

Potassio-niobic fluoride is soluble in 12 to 15 parts of water at

10°: potassio-ilmenic fluoride requires 20 to 30 parts of water at the same temperature for solution. Sodium salts of the niobic acids are perfectly insoluble in liquids containing excess of caustic soda. Sodium salts of the ilmenium acids are slightly soluble in the same liquids.

Niobium and ilmenium may be best prepared in the metallic form by reducing the double potassium fluorides with potassium in a wind furnace, treating the fused mass with water, and drying the insoluble portion over sulphuric acid. The metals are thus obtained as black powders which contain a little hydrogen mechanically retained. When niobium is heated in air it gains 20·49 per cent. in weight, forming M_2O_3. Ilmenium gains 37·96 per cent., forming Il_2O_5. These results differ from those obtained by Marignac. They more nearly agree with Rose's numbers. According to the author, the columbite with which Rose worked contained ilmenium, and the substance regarded by Rose as pelopium chloride was really a mixture of the chlorides of tantalum and ilmenium. Marignac, again, was really working, says the author, with a mixture of niobium and ilmenium, and sometimes even with pure ilmenium: his results, except the crystalline determinations, which hold good for the salts of either metal, are not trustworthy.

The author describes a great many salts of niobium, tantalum, neptunium, and ilmenium. Inasmuch as he takes the atomic weight of the two former as 114·2 and 176 respectively (on what evidence does not plainly appear), he obtains some rather peculiar formulæ. The nomenclature adopted for the oxides and oxyacids of these metals in no way distinguishes between these substances which are true oxides and those hydrated oxides which act as acids. The following are the principal oxides, acids, *salts of these acids*, and haloïd compounds mentioned by the author:—

I. *Oxides.*

Tantalum.	Niobium.	Ilmenium.
TaO	NbO	Il_2O_3
Ta_2O_3	Nb_2O_3 (?)	Il_4O_7
TaO_2	Nb_4O_7	IlO_2
Ta_2O_5	NbO_2	Il_2O_5
TaO_3 (probably meant for $HTaO_3$)	Nb_2O_5, *said to be unknown*	IlO_3($HIlO_3$?)
	NbO_3 ($HNbO_3$?)	

II. *Oxy-salts.*

$K_2O.Ta_2O_5$	$3K_2O.2Nb_2O_3.13H_2O$	$Na_2O.Il_2O_3.7H_2O$
$4K_2O.3Ta_2O_5.16H_2O$	$4K_2O.3Nb_2O_3.16H_2O$	$2Na_2O.Il_4O_7.13H_2O$
$2K_2O.3TaO_3.9H_2O$	$2Na_2O.Nb_4O_7.11H_2O$	$3K_2O.Il_4O_7.15H_2O$
	$3K_2O.Nb_4O_7.11H_2O$	$7K_2O.2Il_4O_7.27H_2O$
	$3K_2O.4NbO_2.13H_2O$	$2Na_2O.3IlO_2.12H_2O$
		$K_2O.IlO_3.3H_2O$
		$2Na_2O.3IlO_3.9H_2O$

III. *Haloïd Compounds.*

Tantalum.	Niobium.	Ilmenium.
$TaCl_5$	$NbCl_3$*	$IlCl_3$
TaF_5†	$NbCl_6$*	$2KF.IlF_3.H_2O$
TaF_6†	Double fluorides, same as ilmenium compounds	$4KF.Il_2F_7.2H_2O$
$2KF.TaF_6$		$2KF.IlF_4.H_2O$
$2KF.TaF_5$		$3KF.IlF_6.H_2O$.

Note by Abstractor.—The author's nomenclature for the niobium, &c., oxides and acids—he calls them all acids except NbO—is as follows:—

Niobium oxide.	Hyponiobous acid.	‡Niobous acid.	Niobous acid.	Hyponiobic acid.	Niobic acid.
NbO	Nb_2O_3	Nb_4O_7	NbO_2	Nb_2O_5	NbO_3 ($HNbO_3$?)

Would not the following be preferable?—

Hyponiobous oxide.	Niobous oxide.	Niobo-hyponiobic oxide.	Hyponiobic oxide.	Niobic oxide.
NbO	Nb_2O_3	Nb_4O_7 (if it exists)	NbO_2	Nb_2O_5

M. M. P. M.

Preparation of Pure Manganese Chloride from Chlorine Residues. By A. Pizzi (*Gazzetta chimica italiana*, vii, 111—113).—The clear liquid is boiled with granulated zinc until the ferric chloride is reduced and the iron precipitated in the metallic state together with any nickel that may be present. The liquid is filtered, sodium acetate and some acetic acid added, and the zinc, lead, and copper precipitated by hydrogen sulphide. On adding ammonium sulphide to the filtrate the manganese and cobalt are thrown down as sulphides; this precipitate after being thoroughly washed is treated with hydrochloric acid, which dissolves the manganese and leaves the cobalt. The solution of pure manganese chloride thus obtained yields pure manganese carbonate, and from this the other salts of manganese may be prepared.

C. E. G.

Presence of Free Ammonia in Cast Steel. By P. Regnard (*Compt. rend.*, lxxxiv, 260—261).—On breaking several ingots of steel made by "Ponsard's method," a decided odour of ammonia was noticed, accompanied by a slight hissing, the latter being very perceptible when the ear was applied against the ingot. The evolution of gas was clearly shown by wetting the fractured surface with soap and water, a frothing resulted, and the volume of gas thus evolved from a single specimen was somewhat greater than one centimeter cube.

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* These chlorides are not generally supposed to exist; the author quotes vapour-density determinations of Deville and Troost. The number quoted for $NbCl_3$ is the same as that obtained by the French chemists for $NbOCl_3$; assuming that oxygen is absent, and that niobium has the atomic weight 114·2, the number agrees with the formula, $NbCl_3$. The number given for $NbCl_5$ is 158. Deville and Troost obtained 138 for the highest chloride of niobium; this agrees with $NbCl_5$, taking 94 as the atomic weight of niobium. The pentachloride, $NbCl_5$, is not mentioned by the author.—M. M. P. M.

† Tantalum hydrates dissolve in hydrofluoric acid to produce these fluorides. This is quite against the generally received statements.—M. M. P. M.

The gas was collected from about one hundred ingots and analysed. It burnt with a scarcely luminous flame, and detonated strongly when mixed with air. It proved to be nearly pure hydrogen, with perhaps a trace of acetylene. No gas was obtained from the metal when it was re-cast previous to being broken.

[The absence both of ammonia and nitrogen from the analysed gas is so remarkable, that it might almost be supposed that the gas had been collected over water. It is not distinctly stated so in the paper, but it certainly seems to be implied that such was the case.—Abs.].

J. W.

Mineralogical Chemistry.

A New Combination of Elba Calcite and a Rare Development of a Crystal of Calcite from Oberstein. By G. vom Rath (*Jahrb. f. Min.*, 1876, 770).—The limestone of Fort Falcone, near Portoferrajo in Elba, is penetrated by numerous veins of calcite, together with beautiful crystals of the same mineral exhibiting the forms $-2R.R$, and the extraordinary scalenohedron, $\frac{3}{2}R\frac{20}{9}$, which has not been observed before. The term "development" is used to express the passing of a crystal into an entirely different form or combination *during its growth.* These developments show either that an interruption must have taken place during crystallisation, or else that the latter must have occurred under different conditions. As an example of such a development the author mentions a calcite crystal found in the melaphyr of Oberstein which exhibits either a rhombohedral or a scalenohedral habit. This crystal is built up of the rhombohedron $-2R$ modified by the extremely rare scalenohedron $-\frac{1}{2}R4$. The rhombohedron is attached by its undermost pole, and in the centre of it is sunk the scalenohedron already mentioned, appearing as a kernel in the crystal. This scalenohedron does not exhibit any combination with $-2R$, but the rhombohedron $-2R$ has been afterwards developed, and exhibits the scalenohedron $-\frac{1}{2}R4$ combined with it; hence there must have been two stages of growth with this crystal, viz., the first purely scalenohedral, the second rhombohedral with scalenohedral modifications.

C. A. B.

The Optical and Thermic Properties of Datholite. By C. Bodeweg (*Jahrb. f. Min.*, 1876, 770—771).—E. Dana had already proved that datholite crystallises in the monoclinic system, and the author thought it would be interesting to seek further confirmation of the truth of Dana's investigations by subjecting a crystal section of datholite (made parallel to the plane of symmetry) to stauroscopic examination. Measurements made by means of the stauroscope showed that the first bisectrix lies in the acute angle of the axes "a" and "c," and forms with the latter the following angles:—

For red light (Li) 3° 51′
" yellow " (Na) 4° 2′
" green " (Tl) 4° 9′

The author then ascertained the change which the angle of the base on the vertical axis undergoes, on increasing the temperature. If datholite were rhombic (the base being the plane of symmetry), this angle would remain constant at all temperatures. This did not prove the case however, as a datholite crystal from Andreasberg gave the following measurements in the heating apparatus:—

OP : ∞ Ᵽ ∞ = 89° 31′ 7″ at 20° C.
89° 28′ 13″ " 126°
89° 27′ 36″ " 130°
89° 26′ 28″ " 222°

At 21° the angle was 89° 29′ 41″. The total variation was therefore 4′ 39″. C. A. B.

The Glaucophane of Zermatt. By C. Bodeweg (*Jahrb. f. Min.*, 1876, 771—772).—In general the crystals show only the prismatic zone, ∞ P. ∞ Ᵽ ∞ Ᵽ ∞, the forms OP and + P occurring only seldom. ∞ P – ∞ P = 124° 44′. Cleavage very complete parallel to ∞ P, the angle being 124° 30′, or that of hornblende. Hardness 6·5; spec. gr. 3·0907. A stauroscopic examination of a section made parallel with the plane of symmetry showed that the chief direction of elasticity (the second bisectrix) lies in the acute angle formed by the crystallographical axes a and c: 4° 24′ for lithium red, 4° 16′ for sodium yellow, and 4° 13′ for thallium green. A section made parallel to ∞ Ᵽ ∞ showed that the optical axes lie in the plane of symmetry The optical characteristics are negative. The mineral is an excellent example of pleochroism. Before the blowpipe it fuses easily to a greyish-white glass. Its mean composition is as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	
57·81	12·03	2·17	5·78	13·07	2·20	7·33	= 100·39

Glaucophane is an isomorphous mixture of the following bisilicates, Na_2SiO_3, $CaSiO_3$, $MgSiO_3$, $FeSiO_3$, $Al_2Si_3O_9$, $Fe_2Si_3O_9$.

The gastaldite of Strüver is completely isomorphous with the glaucophane of Syra and Zermatt, containing however a large amount of aluminium bisilicate. C. A. B.

The Glaucophane and Glaucophane-bearing Rocks of the Island of Syra. By Otto Luedecke (*Jahrb. f. Min*,, 778—780, 1876).—From the microscopical and chemical examinations of the above-mentioned mineral, the author concludes that it must be classed with arfvedsonite, achmite, and aegerine; its constitution corresponding with the formula—

$$\begin{array}{l} 3Na_2SiO_3 \\ 6RSiO_3 \\ 3Al_2Si_3O_9 \\ Fe_2Si_3O_9 \end{array}$$

R = Fe, Mn, Mg, Ca. Glaucophane fuses before the blowpipe to a non-magnetic enamel, its hardness is that of hornblende. Sp. gr. = 3·101—3·113. It is strongly pleochromatic, absorbs light, and corresponds closely with hornblende crystallographically; occurring in a similar way to that mineral as a constituent of rocks. In the glaucophane-eclogites the smaragdite is replaced by glaucophane. Glaucophane-slate is also observed at Syra, and also mica-slate containing glaucophane as an accessory.

Glaucophane-eclogite consists principally of glaucophane, omphacite and garnet, with muscovite and quartz as secondary constituents, and approaching nearly to the eclogites of von Drasche. *The mica-slate* is found in two modifications, one consisting of parallel layers of muscovite and quartz, with numerous glaucophane prisms and small garnets as accessories; the other in quartzose, consisting of many layers of quartz one meter thick, separated by thin films of muscovite, the accessories glaucophane and garnet being isolated. *The eclogite-mica-slate* unites the constituents of glaucophane-eclogite and mica-slate. It consists of thin parallel layers of muscovite enclosing ellipsoidal quartz masses and glaucophane, omphacite and garnet. *Glaucophane-slate* was formerly described as a disthene-rock, but is now found to consist of parallel layers of glaucophane separated by white or greenish muscovite, with epidote and hematite as accessories. Virlet described rocks intermediary between glaucophane-eclogite and glaucophane-slate (poor in mica), to which Luedecke assigned the names omphacite-zoisitegabbro and epidote-glaucophane. The first consists of omphacite and zoisite, has a granular structure, with talc, muscovite, epidote, tourmaline and calcite as accessories; the second is a granulur mixture of epidote and glaucophane, with omphacite, zoisite and garnet as accessories. *Glaucophane-zoisite-omphacite-rock* consists of the three minerals included in its name; there is also a slate having the same composition. *Smaragite-chlorite-rock* is a granular mixture of smaragdite and chlorite with glaucophane, epidote and garnet. The crystalline limestone which covers the mica-slate contains mica and glaucophane.

C. A. B.

The Syenite Mountains of Ditro. By G. VOM RATH (*Jahrb. f. Min.*, 772—773, 1876).—The finest varieties of these rocks are undoubtedly the nepheline-syenite (miascite) and the sodalite-syenite (ditroite). The miascite constitutes the greater part of the rocks, and consists of greyish nepheline, white orthoclase and oligoclase; black hornblende with biotite, zircon, titanite, magnetite, and iron-pyrites. Structure coarse-grained to fine-grained. The nepheline always occurs in irregularly formed grains. In some specimens nepheline and orthoclase predominate, whilst in others hornblende occurs in crystals attaining a size of 3 cm. The hornblende is partially intergrown with biotite plates or enveloped by them. Titanite occurs in large amount, often unevenly distributed in the specimens rich in hornblende, some crystals occasionally attaining a length of 8 mm. with predominating pyramid, the "habit" being that peculiar to syenitic titanite. Typical miascite does not include sodalite as a normal constituent, but it occurs in certain varieties of it as an accessory, the amount increasing sometimes until it becomes a definite constituent, together with nepheline, resulting in the formation of ditroite. In addition to the orthoclase and sodalite, ditroite contains oligoclase, nepheline, hornblende, biotite, zircon, titanite, cancrinite, pyrochlor, magnetite and iron-pyrites. The orthoclase is whitish or yellowish in colour, attains occasionally a size of 8 cm., and resembles that in the Laurvig syenite, it is also penetrated by plagioclase. The oligoclase occurs in isolated grains or is regularly interpolated with the orthoclase. The sodalite possesses a beautiful light or dark blue colour, is not crystallised, and occurs in veins. The mean of several analyses showed ditroite to have the following percentage composition:—

Cl.	SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	Na.	H_2O.	
6·08	38·66	32·81	0·95	1·04	13·28	3·93	2·36	= 99·11

Cancrinite occurs in ditroite in pebble-like, light-red coloured grains; the occurrence of this mineral with sodalite is also observed at Miask, Brevig, and Lichfield, whilst the rocks of these localities closely resemble ditroite. Black biotite displaces hornblende in specimens rich in sodalite, whilst brown coloured zircon crystals of the common form partially replace the titanite. The pyrochlor occurs in very small, brown, shining grains. Ditroite does not penetrate the miascite in veins, but occurs rather as a local modification of the latter, its distribution being irregular. C. A. B.

Pyrargyrite from Andreasberg. By G. vom Rath (*Jahrb. f. Min.*, 1876, 774).—The author observed the following forms occurring in this specimen, viz.: $R \,.\, -\frac{1}{2}R \,.\, \frac{1}{5}R^{\frac{11}{3}} \,.\, \frac{1}{4}R^3 \,.\, \frac{1}{5}R^5 \,.\, \frac{1}{5}R^7 \,.\, \frac{2}{3}R_{\frac{8}{3}} \,.\, R^3 \,.\, R^5 \,.\, \infty P2 \,.\, \infty R$. Of the seven scalenohedrons $\frac{1}{5}R^{\frac{11}{3}}$ and $\frac{2}{3}R_{\frac{8}{3}}$ are new, and their measurements are as follows:—

	Short terminal edge.	Long terminal edge.
$\frac{1}{5}R^{\frac{11}{3}}$	140° 28′	160° 33′
$\frac{2}{3}R_{\frac{8}{3}}$	113° 3′	150° 59′

Note by Abstractor.—The scalenohedron $\frac{2}{3}R_{\frac{8}{3}}$ is mentioned (as having been observed on pyrargyrite crystals) in the fifth edition of Dana's "System of Mineralogy," 1868. C. A. B.

Hydrotitanite (a new Mineral). By George König (*Jahrb. f. Min.*, 1876, 774).—The crystals of perowskite from Magnet Cove, Arkansas, often contain greyish, soft particles, occasionally consisting entirely of this grey substance. The sp. gr. of the latter is 3·681, therefore 0·2 less than that of the original mineral. On analysis the grey substance was found to have the following composition:—

TiO_2.	Fe_2O_3.	MgO.	CaO.	H_2O.	
82·82	7·76	2·72	0·80	5·50	= 99·60

It will be seen that a remarkable change has occurred in the composition of the original mineral, almost all the calcium oxide and some ferric-oxide being eliminated. C. A. B.

Beryll from Eidsvold, Norway. By WEBSKY (*Jahrb. f. Min.*, 1876, 774).—The crystals examined by the author were emerald-green in colour, embedded in felspar, quartz, or mica. They exhibited the twelve-sided pyramid $\frac{13}{2}P\frac{13}{11}$ in addition to the forms $\infty P \,.\, 0P \,.\, 2P2 \,.\, P$. C. A. B.

Relative Composition of Ulexite and Franklandite. By H. HOW (*Chem. News*, xxxv, 189).—Reynolds (*Phil. Mag.*, April, 1877, 286) describes a new mineral borate found with ulexite in Tarapaca, Peru, which he names franklandite. In comparing the composition of the two minerals the author points out that Reynolds has adopted the wrong formula for ulexite. The correct formula for the latter being $Na2O,2CaO,5B_2O_5$, $15H_2O$, and not $Na_2O,2CaO,6B_2O_3,18H_2O$, as given by Rammelsberg, and shown to be incorrect by Lunge. Reynolds' empirical formula of franklandite, $2Na_2O,2CaO,6B_2O_3,15H_2O$, differs from the author's formula for uxelite by having in excess $Na_2O,2B_2O_3$. How's formula for ulexite being universally received as correct, it follows that the difference between ulexite and franklandite is not, as Reynolds gives it, "that the substitution of one molecule of Na_2O for three molecules of water is capable of converting ulexite into franklandite, as far as composition is concerned," but that the latter differs from the former by containing one molecule of $Na_2O.B_2O_3$ in addition. D. B.

Scottish Tripolite. By W. M. PATERSON (*Chem. News*, xxxv, 151).—The author received a sample of a substance which, under the microscope, appeared to consist almost entirely of fossil or sub-fossil diatomaceæ. The sample was supposed to be a sample of clay having a greyish-white colour and being very light in weight. On calcination the colour, evidently due to a trace of organic matter, disappeared, leaving behind a purely white powder. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Loss on ignition.
95·66	3·08	trace	0·28	1·25 = 100·27

The sample readily dissolved to the extent of 92·4 p. c. in solution of potassium hydrate. From its analysis it will be seen that this substance varies considerably from the celebrated Barbadoes tripolite or that from Sweden (*Chem. News*, xxxiv, 108). Its composition agrees very closely with that from the Puy de Dôme, France, found by Fournier to contain $SiO_2 = 87·2$, Al_2O_3 and $Fe_2O_3 = 2·8$, and $H_2O = 10·0$. If the above were calcined it would be composed as follows, agreeing closely with the Scotch sample:—$SiO_2 = 97·0$; Al_2O_3 and Fe_2O_3 3·0.

The deposit from which the above sample was taken occurs on Ciste Mairearad, one of the highest of the Grampians, on the Glen Feshie side, Inverness-shire. Its extent is unknown, but the sample was taken from a spot where about an acre of it is exposed, varying from

1 to 4 feet in depth, containing no stones or gravel and very little sand. The author hopes to get more information concerning this deposit. D. B.

Investigation of the Manganese Ores of Bukowina.

By Th. Morawski and J. Stingl (*J. Prakt. Chem.* [2], xv, 228—239).—The manganese ores of Bukowina may be divided into eight groups:—

1. Bluish-black masses, spec. grav. = 4·435; hardness, 5—6; contains 85·65 p. c. MnO_2.
2. Kidney-shaped, compact masses, without lustre; spec. grav. 4·471; hardness, that of felspar; contains 81·8 p. c. MnO_2.
3. Stalactitic incrustation; spec. grav. 3·882; hardness, 5—6; MnO_2 = 80·20 p. c.
4. Small kidney-shaped masses; fracture, conchoidal; fractured faces, like graphite; spec. grav. 3·979; hardness, 5—6; MnO_2 = 75·72 p. c.
5. Homogeneous compact masses, of bluish-black colour, with semimetallic lustre; spec. grav. 4·027; hardness, 5—6; MnO_2 = 72·81 p. c.
6. Porous, impure masses, containing 41·66 p. c. MnO_2.
7. Lamellar masses; spec. grav. 2·661; MnO_2 = 8·13 p. c.
8. Rhodonite; distinctly crystalline, pink mass; spec. grav. 3·624; hardness, 5—6; difficultly attacked by acids.

The ores 1 to 5, after deduction of impurities, have a relation of metal to oxygen about 1 to 1·7, nearly that of psilomelane, which is 3 to 5. The authors therefore conclude that the ore is not impure dioxide, but is really a substance of the formula Mn_3O_5.

By treating potassium sulphocyanide with permanganate they obtained violet crystals, with the investigation of which they are still occupied. W. R.

Ardennite. Separation of Vanadic Acid from Alumina and Ferric Oxide.

By A. Bettendorff (*Pogg. Ann.*, clx, 126—131).—In the analysis of ardennite the author now takes advantage of the fact, that when a solution containing alumina and vanadic acid is decomposed by ammonia a yellow precipitate of aluminium vanadate, insoluble in excess of ammonia, is produced. When ammonium phosphate is added to the precipitate and the mixture warmed over the water-bath a reaction occurs by which white insoluble aluminum phosphate is produced, while the supernatant liquid contains ammonium vanadate in solution. In presence of oxide of iron the like reaction also occurs. The precipitate must be washed by decantation. Analyses of two specimens of ardennite in which this mode of separation was adopted gave the following results:—

	No. 1.	No. 2.
Silicic acid	27·50	27·84
Alumina	22·76	24·22
Oxide of iron	1·15	
Oxide of manganese	30·61	26·70
Lime	1·83	2·17
Magnesia	1·38	3·01
Copper	0·17	0·00
Vanadic acid	0·53	9·20
Arsenic acid	9·33	2·76
Water	5·13	5·01
	100·39	100·91

R. R.

The Composition of Speis-cobalt. By C. Rammelsberg (*Pogg. Ann.*, clx, 131—137).—The author controverts a statement of Groth's, which is to the effect that speis-cobalt has properly the composition represented by RAs_2, and that while analytical results do not agree with this, it is because the samples analysed were impure and contained more or less of the two other bodies, RAs and RAs_3. Rammelsberg contends that to make this supposition square with the figures he obtained himself in an analysis of speis-cobalt, the crystals must have contained 53 per cent. of RAs, which cannot be admitted. The two compounds, RAs and RAs_3, are also merely hypothetical, and for these and other reasons he considers Groth's assertion to be destitute of support from facts. R. R.

Analysis of the "Tempelbrunnen" at Rohitsch. By M. Buchner (*Chem. Cent.*, 1876, 789).—The water rises from limestone. Temperature of air = 12° R., temperature of water = 8·4° R.

Total solids in 100,000 parts = 102·2355:—

K_2SO_4.	Na_2SO_4.	$NaNO_3$.	NaCl.	NaI.
0·3616	19·6068	0·1187	1·6950	0·0013

Na_2CO_3.	$CaCO_3$.	Ca_32PO_4.	$MgCO_3$.	$FeCO_3$.
7·6777	7·1842	0·0092	22·5422	0·0486

$AlPO_4$.	SiO_2.	CO_2 half combined.	Free CO_2.
0·0095	0·3307	18·1593	24·4907

M. M. P. M.

The Salts of the Algerian Marshes. By H. le Chatelier (*Compt. rend.*, lxxxiv, 396—398).—The salts which encrust the surface of the earth in the most depressed part of the Algerian sahara, were found by the author to include sodium chloride and sodium sulphate. The non-existence of sodium carbonate is not demonstrated by its absence from their solution, for being found mixed with gypsum and sand, their treatment with water would give rise to a reaction between the sodium carbonate and the calcium sulphate, so that the sodium would be found in the solution in the state of sulphate. A similar reaction between water holding in solution sodium chloride and gypsum in the ground, accounts, he believes, for the efflorescences of sodium sulphate, the calcium chloride produced by the reaction finding its way by diffusion towards the moister strata beneath. The author considers the existence of these salts in the Algerian marshes is not due to the drying up of a former sea, but that the source of the sodium chloride is the masses of rock-salt which exist in the mountains. From these the salt is dissolved out by rain or by subterranean waters, and the saline solution percolates the soil to feed the artesian reservoirs which underlie the desert. R. R.

The Chrome Ores of Greece. By X. LANDERER (*Chem. Centr.*, 1876, 590—591).—In the serpentine rocks of the islands of Eubœa, Sinos, and Paros, in the Peloponesus, near Corinth, and in Phtiotis, rich deposits of chrome iron ore have been found, containing frequently 24 to 48 p. c. of chromium oxide. W. R.

Platinum Ore from the Ural Mountains. By SERGIUS KERN (*Chem. News*, xxxv, 88).—The platinum ores of the Nishni-Tagil and Goroblagodatsky districts, contain notable quantities of foreign metals of the platinum group, with the exception of ruthenium, which occurs only in traces. The amount of platinum varies from 71·2—89·05 per cent., rhodium from 1·05—4·6, and iron, 3·4—13·4. The ore is not refined in Russia, but is sold at a low price to England and France, whence it returns as crucibles, &c., at a high price. In Russia, French crucibles are preferred to English, but the author considers the platinum of the English crucible to be of a higher quality and purer, containing copper as traces, and iron to the amount of ·002 per cent., whereas the French crucibles contain copper (0·22—0·67 per cent.), and iron (0·3 per cent.). E. W. P.

The Neuntmannsdorf Meteoric Iron of the Dresden Museum. By F. EUGEN GEINITZ (*Jahrb. f. Min.*, 1876, 608—612).—This specimen was found in 1872. It is round, originally weighed 25 lbs.; it is malleable, and its surface is covered with a film of blackish-brown oxide, its greatest peculiarity being the fluid reddish exudation occurring on the surface, and the exfoliation of the oxidised outer film. The colour of this meteoric iron is iron-grey, polished and etched surfaces not exhibiting Wiedmannstätts' figures. A selected portion was analysed, and found to have the following percentage composition:—

Iron..................	93·04
Nickel...............	6·16
Phosphorus...........	0·22
	99·42

Specific gravity, 6·21. In the mass of meteoric iron were observed numerous, well defined, round lumps, or occasionally straight, narrow strips of a brittle, lustrous substance, having a light pinchbeck brown colour, and a specific gravity, 3·98. These lumps consist entirely of iron and sulphur, in the following amounts per cent.:—

Iron	63·80
Sulphur	37·36
	101·16

No nickel was detected. Besides the round lumps described above, two or three crystals having a very strong lustre were observed on an etched piece of the iron, but they did not differ in composition from the lumps; and as the latter, according to all appearance, consist of troïlite, the author considers this the first evidence of *crystallised* troïlite ever observed. The meteorite is covered here and there at the ordinary temperature with the brownish-red fluid exudation already mentioned, some spots being richer in this exudation than others, whilst some are entirely free from it. Sometimes also a film of oxide is formed around the small troïlite nodules, by the action of this exudation. An analysis of the fluid proved it to contain ferric and ferrous chloride, but no traces of sulphuric acid or phosphorus compounds could be detected. The author considers the "weathering" of the meteorite to be caused by the presence of *enclosed* ferrous chloride, which, taking up moisture, and acting upon the free iron surrounding it, is converted into a mixture of ferrous and ferric chlorides; whilst a portion of iron separates out, and forms the outer exfoliating coating of ferric oxide already referred to.

Nordenskjöld (*Geol. Mag.*, ix, 516) observed from 0·16 to 1·16 per cent. of chlorine in the Ovifak "meteoric iron," and a trace of ferrous sulphate, also calcium chloride, whilst a similar greenish fluid exudation occurred upon the surface. W. Flight ("A Chapter in the History of the Meteorites, *Geol. Mag.*, xii, 1875) also observed an exudation on several "meteoric irons" (particularly those of Staunton, Virginia, Lancé and Anthon, France), which contained iron, chlorine and nickel. There are instances of a similar occurrence in other specimens, and the author concludes from his observations, and those of Flight, Nordenskjöld, and Buchner, that the chlorine contained in "meteoric iron," is a constituent only of accessory compounds.

C. A. B.

Organic Chemistry.

Solubility of Ether in Aqueous Hydrochloric Acid. By H. N. DRAPER (*Chem. News*, xxxv, 87).—Ether having a density of 0·725 at 14° is insoluble in a saturated solution of calcium chloride, but is dissolved by distilled water at 11° in the ratio of 100 vols. to 10 vols., and by experiment it is found that 100 vols. of ether at 12° dissolve 2 vols. of water; this is somewhat different from the general statement, which is that the solubility of water in ether is 1 in 10. When 50 vols. of ether are mixed with 50 vols. of aqueous hydrochloric acid (sp. gr. 1·196 at 14°) contraction to 95 vols. takes place, and a thin, oily, fuming liquid is produced having a sp. gr. of 1·010 at 14°; thus hydrochloric acid of 38·52 per cent. will dissolve more than its own volume of anhydrous ether. The temperature appears to have a much greater effect upon the solubility than in the case of any other two fluids, for the capacity of hydrochloric acid for ether is nearly one-third greater at 0° than at 38°, the ether separating as the temperature is raised, in minute bubbles, which are not easily redissolved so long as the liquid remains quiet, but are immediately dissolved on agitation if the temperature be lowered. No chemical action takes place, and the solvent power of the acid is directly proportional to its strength. The following table represents the amount of ether dissolved at the corresponding temperature:—

Temperature centigrade.	Vols. of ether dissolved.	Temperature centigrade.	Vols. of ether dissolved.
− 16°	185·0	16°	162·5
0°	177·5	21°	157·5
+ 8°	172·5	27°	150·0
9°	170·0	32°	142·5
10°	167·0	38°	135·0

E. W. P.

Dichloracetic Acid. By C. O. CECH and P. SCHWEBEL (*Deut. Chem. Ges. Ber.*, x, 288—290).—The authors prepare this substance by heating its ethyl-ether (obtained by the action of dry potassium cyanide on chloral hydrate in alcoholic solution) with strong hydrochloric acid in a retort with reversed condenser.

Dichloracetic and aniline combine, with evolution of heat, forming a solid mass, which dissolves in alcohol and crystallises therefrom in delicate yellowish needles, melting at 125° and agreeing in composition with the formula, $C_6H_7N.C_2H_2Cl_2O_2$.

Aniline dichloracetate is decomposed by strong soda-ley, even in the cold, aniline being set free and dichloracetic acid reproduced. But when it is boiled with weak soda-ley the reaction just mentioned is accompanied by another, in which phenyl isocyanide is formed, together with hydrochloric and formic acids, according to the equation—

$$C_6H_7N.C_2H_2Cl_2O_2 = CN.C_6H_5 + 2HCl + CH_2O_2.$$

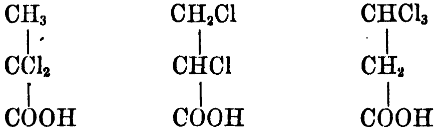
J. R.

A Simple Method of obtaining Propionic Acid from Propionitril. By H. BACKUNTS and R. OTTO (*Deut. Chem. Ges. Ber.*, x, 262).—This method is founded on the fact that propionitril is readily decomposed by sulphuric acid of a certain strength, and that the propionic acid thereby produced is insoluble in the solution of ammonium sulphate formed at the same time.

The authors operate thus:—Propionitril (50 grams) is heated in the water-bath to about 100° with 150 grams of a mixture of 3 vols. of sulphuric acid and 2 vols. of water. The reaction is complete in about two hours. After allowing the liquid to cool to 50°, the colourless and nearly pure propionic acid is separated and freed from traces of water and ammonium sulphate by rectification. The yield is almost quantitative. J. R.

On the Dichloropropionic Acids formed from Dichloropropionitril.

By H. BACKUNTS and R. OTTO (*Deut. Chem. Ges. Ber.*, ix, 1876—1881).—Three dichloro-substitution-products of propionic acid are possible, viz.:—



$$\begin{array}{ccc} CH_3 & CH_2Cl & CHCl_3 \\ | & | & | \\ CCl_2 & CHCl & CH_2 \\ | & | & | \\ COOH & COOH & COOH \end{array}$$

α. β. γ-dichloropropionic acid.

Till a short time ago the second only was known.

Preparation of α-Dichloropropionic Acid.—One part of α-dichloropropionitril is heated with 2 to 3 parts of a mixture of equal volumes of concentrated sulphuric acid and water to about 120°. The reaction is over when the oily layer which floats on the sulphuric acid no longer boils. The oily layer is removed on cooling, and the acid rectified. If the quantity of sulphuric acid employed is too great, or if the acid is too much concentrated, decomposition-products are formed at the same time. α-dichloropropionic acid boils at 185 to 190°, and remains liquid at —8°: it may be distilled alone or with steam without separation of hydrochloric acid.

Salts of α-Dichloropropionic Acid.—These were prepared by addition of the bases or their carbonates to a solution of the acid in water or alcohol. With the exception of the silver-salt, they are stable when dry at ordinary temperatures, but are decomposed when heated, with formation of a metallic chloride. The solutions of the salts also undergo the same change when warmed, especially if they contain an excess of base. These salts are generally soluble in water and in alcohol.

Potassium Salt, $C_3H_3Cl_2KO_2 + 6H_2O$.—Brilliant needles or tufts; decomposed at 60° to 70°.

Ammonium-salt, $C_3H_3Cl_2(NH_4)O_2$.—Thin, white, fatty laminæ.

Silver-salt, $C_3H_3Cl_2AgO_2$.—Small white needles, soluble with difficulty in water; decomposed at ordinary temperatures.

Calcium-salt, $(C_3H_3Cl_2O_2)_2Ca + 3H_2O$.—White, sheaf-like needles, with glassy or silky appearance; decomposed at 120°.

Barium-salt, $(C_3H_3Cl_2O_2)_2Ba + H_2O$.—Glassy, rhombic laminæ, which lose their water of crystallisation at 80° and become opaque.

Zinc-salt, $(C_3H_3Cl_2O_2)_2Zn + H_2O$.—Transparent needles resembling the sulphate; they lose their water of crystallisation at 60°, and are decomposed at 80°.

The ethers of α-dichloropropionic acid are easily prepared by the action of hydrochloric acid on the solution of the acid in the corresponding alcohol.

The *methyl-ether* is a colourless liquid with fruity odour: boils at 143° to 144° (uncorrected).

Ethyl-ether.—Identical with the ether formed from α-dichloropropionitril and alcohol in presence of sulphuric acid. Boils at 156° to 157°.

Allyl-ether.—A faint yellow liquid, which is decomposed on distillation with separation of hydrochloric acid: fruit-like smell. Boils at 176° to 178°.

Isobutyl-ether.—Like the foregoing: not completely decomposed at 183° to 185°: pleasant pine-apple smell.

Starting from the methyl-ether, the boiling points of these ethers rise by intervals of about 10°.

Behaviour of α-Dichloropropionic Acid to Nascent Hydrogen.—By the action of zinc and dilute sulphuric acid at ordinary temperatures, the acid is converted into propionic acid. The ethyl-ether of α-dichloropropionic acid is also converted by similar treatment into the ethyl-ether of propionic acid.

Conversion of α-Dichloropropionic Acid into Monochloracrylic Acid.—The aqueous solution of the silver-salt of α-dichloropropionic acid becomes turbid at ordinary temperatures, and gradually deposits the whole of the silver as chloride. The change is completed in a few minutes by boiling. The filtrate from the silver chloride contains an acid of the composition of monochloracrylic acid. It may be formed thus: $C_3H_3Cl_2AgO_2 = C_3H_3ClO_2 + AgCl$. The dry silver-salt, even in closed vessels, suffers the same change at ordinary temperatures.

The potassium salt of monochloracrylic acid may also be obtained by heating an alcoholic solution of α-dichloropropionic acid (one molecule) with a solution of potassium hydrate (two to three molecules). This acid is not identical with the β-monochloracrylic acid of Werigo and Werner, but corresponds with the α-monobromacrylic acid of Philippi and Tollens.

Conversion of α-Dichloropropionic Acid into Acetic and Carbacetoxylic Acids.—When an aqueous solution of α-dichloropropionic acid is heated with freshly precipitated silver oxide, the following change takes place:—

$$\underset{\text{Silver α-dichloropropionate.}}{C_3H_3Cl_2AgO_2} + 2Ag_2O = 2AgCl + 2Ag + CO_2 + \underset{\text{Silver acetate.}}{C_2H_3AgO_2}.$$

By treating an aqueous solution of α-dichloropropionic acid with silver carbonate, a salt was obtained in small brown needles which the authors believe to be the silver-salt of carbacetoxylic acid.

G. T. A.

Conversion of α-Dichloropropionic Acid into Monochloracrylic and Pyroracemic Acids.

By H. Backunts and R. Otto (*Deut. Chem. Ges. Ber.*, x, 264—266).—An aqueous solution of the silver-salt of α-dichloropropionic acid is converted by boiling for a few minutes into a solution of monochloracrylic acid, silver chloride being deposited:

$$C_3H_3Cl_2AgO_2 = C_3H_3ClO_2 + AgCl.$$

On heating the latter solution with silver oxide or (better) carbonate for some hours, the silver salt first formed is again decomposed, and pyroracemic acid is produced in accordance with the equation—

$$\underset{\text{Silver chloracrylate.}}{C_3H_2ClAgO_2} + H_2O = \underset{\text{Pyroracemic acid.}}{C_3H_4O_3} + AgCl.$$

These two decompositions are effected in one operation by simply heating a solution of α-dichloropropionic acid with an equal number of molecules of silver carbonate till silver chloride is no longer formed, when the following reaction takes place:

$$C_3H_4Cl_2O_2 + Ag_2CO_3 = C_3H_4O_3 + 2AgCl + CO_2.$$

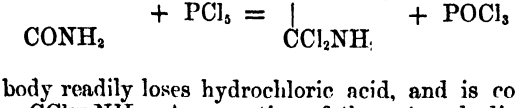
J. R.

Solid Dichloropropionitril. By H. BACKUNTS and R. OTTO (*Deut. Chem. Ges. Ber.*, x, 263).—In the action of chlorine on propionitril, there is formed, besides the liquid α-dichloropropionitril, a solid product having the same composition, which crystallises from alcohol in rhombic tables melting at 73·5° This latter body is a polymeric modification of liquid α-dichloropropionitril, as is shown by the fact that, when heated with dilute sulphuric acid, it is almost entirely converted into α-dichloropropionic acid, $CH_3—CCl_2—COOH$, boiling at 185—190°, thus behaving in the same manner as liquid α-dichloropionitril when similarly treated.

The solid product is formed in larger quantity the lower the temperature at which chlorine acts upon propionitril. J. R.

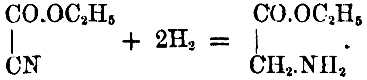
Aconitic Acid in the Juice of the Sugar-cane. By ARNO BEHR (*Deut. Chem. Ges. Ber.*, x, 351—355).—In the juice of the sugar-cane the author finds aconitic acid, $C_6H_6O_6$, which, he points out, may correspond in the sugar-cane with the citric acid, $C_6H_8O_7$, that accompanies sugar, $C_6H_{12}O_6$, in beet-root. R. R.

Action of Phosphorus Pentachloride on Acid-Amides. By O. WALLACH (*Liebig's Annalen*, clxxxiv, 1—127).—On mixing equal numbers of molecules of oxamethane and phosphorus pentachloride, a reaction sets in which is quickened by gentle heating. A liquid is obtained from which on standing or cooling crystals are deposited. To isolate these, the product is mixed with twice its volume of dry petroleum-naphtha, which precipitates the crystalline body, while phosphorus-compounds remain in solution. The crystals, after being washed with petroleum, are dried on a porous plate over calcium chloride or soda-lime. The analysis showed that first the compound $C_4O_2H_7Cl_2N$ is formed:



$$\begin{matrix}COOC_2H_5\\ \\ CONH_2\end{matrix} + PCl_5 = \begin{matrix}COOC_2H_5\\ |\\ CCl_2NH\end{matrix} + POCl_3$$

but this body readily loses hydrochloric acid, and is converted into $COOC_2H_5—CCl{=}NH$. A separation of these two bodies was found impossible; the needles obtained by precipitation with petroleum-naphtha dissolve readily in benzene or chloroform; water acts violently and re-converts them into oxamethane, which is also produced by aqueous ammonia, but soon ammonium oxamate separates out. The chlorine-product dissolves with the evolution of heat, in aniline, a crystalline compound being formed consisting probably of $CONHC_6H_5.—C(NC_6H_5)—NHC_6H_5$. On heating the chlorides above their melting points, hydrochloric acid is given off, and almost pure ethyl cyanocarbonate distils over; 50 grams of amethane yielding 20 grams of this compound, while Weddige, by using oxamethane and phosphorus pentoxide, obtained only 20—25 per cent. By adding hydrochloric acid very gradually to a mixture of an alcoholic solution of cyancarbonic ether and zinc, glycosine is formed—



$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CN \end{array} + 2H_2 = \begin{array}{l} CO.OC_2H_5 \\ | \\ CH_2.NH_2 \end{array}.$$

This ethyl-ether thus obtained decomposing, as is known, on the evaporation of its solution into alcohol and glycocine.

From the petroleum-naphtha which has been used for separating the chlorides, large prisms separate out on standing, consisting of $C_4H_6O_3Cl_4NP$. They melt at 128—130°, dissolve freely in ether, benzene, and chloroform, but sparingly in petroleum. They dissolve but slowly in water and acids, readily in alkalies; on heating them they are resolved into phosphorus oxychloride, ethyl cyanocarbonate, and hydrochloric acid. Their constitution seems therefore to be $COOC_2H_5—CCl_2(NH)POCl_2$, which, however, does not explain why they are only formed in the presence of a little water.

Benzamide and phosphorus pentachloride act on each other slowly, and yield hydrochloric acid, phosphorus oxychloride, and benzonitril. But if the mixture be gently heated as soon as it begins to liquefy, and then strongly cooled, crystals are formed, which were dried over soda-lime. They evolve hydrochloric acid on exposure to the air, are quickly decomposed by water, and contain phosphorus.

On heating acetamide and phosphorus pentachloride in a flask connected with an inverted condenser, an almost clear liquid is obtained, which on distillation yields acetonitril, phosphorus trichloride, and oxychloride, while a brown mass remains behind.

Phosphorus pentachloride at a gentle heat acts violently on trichloracetamide, hydrochloric acid and a little free chlorine being evolved. After cooling a crystalline mass was obtained, which, after washing with a little petroleum, was found to consist of C_2Cl_6ONP; it is probably formed by the following reactions:

$$\begin{array}{lcl} CCl_3.CONH_2 + PCl_5 & = & CCl_3.CCl_2NH_2 + POCl_3 \\ CCl_3.CCl_2NH_2 + POCl_3 & = & CCl_3.CCl_2(NH)POCl_2 + HCl \\ CCl_3.CCl_2(NH)POCl_2 & = & CCl_3.CCl{=}NPOCl_3 + HCl. \end{array}$$

The freshly prepared compound melts at 78—81°, and distils at 255—259°; its vapours attack the mucous membranes. It cannot be recrystallised, or kept, without undergoing decomposition.

Dichloracetamide yields a similar but even more unstable compound, which crystallises well and has the composition C_2HCl_5NOP. Phosphorus pentachloride and monochloracetamide appear to yield, amongst other products, phosphorous trichloride, and the compound $C_2H_2Cl_4NOP$, while phenylacetamide and phosphorus pentachloride from α-toluylnitril, phosphorus, oxychloride and trichloride.

Diethyloxamide is most conveniently prepared by the action of aqueous ethylamine on ethyl oxalate. On mixing one molecule with two molecules of phosphorus pentachloride a reaction soon sets in, and a clear liquid is obtained, containing the compounds—

$$\begin{array}{l} CCl_2N(C_2H_5)H \\ | \\ CCl_2N(C_2H_5)H \end{array} \quad \text{and} \quad \begin{array}{l} CCl = NC_2H_5 \\ | \\ CCl = NC_2H_5 \end{array}$$

for on adding water, diethyloxamide is again formed. But if the product be gently heated or kept for a few days in a well-closed vessel, a dark brown liquid is formed, yielding with water no diethyloxamide.

On removing the phosphorus oxychloride by distilling under a diminished pressure, a crystalline hydrochloride of a base remains behind, which was dissolved in a little water and neutralised with sodium carbonate in order to remove free hydrochloric and phosphoric acids. The solution was then evaporated on a water-bath, the residue exhausted with absolute alcohol, which was distilled off and the impure hydrochloride distilled with solid caustic potash. First ethylamine distilled over, and then an oil having a narcotic smell and a strongly alkaline reaction. It boils at 217—218°, solidifies at a low temperature to crystals melting again at the common temperature, and having at 15° the specific gravity 1·142. It is more freely soluble in cold water than in warm, like conine, has the composition $C_6H_9ClN_2$, and may be called *chloroxalethyline*.

Its hydrochloride, $C_6H_9ClN_2.HCl$, crystallises from an aqueous solution in needles containing one molecule of water. On standing over sulphuric acid it becomes anhydrous, and is converted into a crystalline, very hygroscopic mass. From alcohol it crystallises in prisms; it readily sublimes, and can be distilled without decomposition. $(C_6H_9ClN_2.HCl)_2PtCl_4$ crystallises from dilute alcohol in well defined prisms. The nitrate and sulphate dry up to viscid masses. $C_6H_9ClN_2.C_2O_4H_2$ is obtained in white needles by adding ether to an alcoholic solution of the base and oxalic acid. The picrate forms yellow needles.

Chloroxalethyline forms also metallic compounds. $(C_6H_9ClN_2)NO_3Ag$ is obtained by adding silver nitrate to an aqueous solution of the base, as a thick white precipitate crystallising from hot alcohol in thick prisms. $C_6H_9ClN_2.HgCl_2$ is a white precipitate crystallising from dilute alcohol in small white needles. It is freely soluble in acids. If concentrated solutions of chloroxalethyline hydrochloride and mercuric chloride be mixed, a precipitate is sometimes formed at once, but generally on standing, needles separate out consisting of $C_6H_9ClN_2.HCl + 4HgCl_2$. An aqueous solution of the base yields also the following precipitates:—

Mercurous nitrate: white, voluminous.
Mercuric cyanide: white, crystalline.
Stannous chloride: white.
Auric chloride: yellowish-brown.
Copper sulphate: after some time or on heating, blue.
Thallium chloride: white, soon turning brown.
Ferric chloride: brown.
Ferrous sulphate: bluish-green.
Cobalt nitrate: violet.
Iodine and potassium iodide: brown.
Potassium-mercuric iodide: white.
Phosphomolybdic acid: yellow.
Ammonium molybdate: white.
Tannin: white.

When chloroxalethyline is mixed with methyl iodide, a violent reaction soon sets in, $C_6H_9ClN_2.CH_3I$, being formed, which crystallises in white prisms or needles. On boiling it with caustic potash, ethylamine is given off. The iodide treated with an alcoholic solution of iodine, yields a crystalline periodide, and forms a similar compound with bromine. On treating the iodide with moist silver oxide, the very alkaline hydroxide is formed. $C_6H_9ClN_2.C_2H_5I$, crystallises in deliquescent plates. $C_6H_9ClN_2.C_2H_5Br$ is formed only when its constituents are heated to 100°, and crystallises in very hygroscopic needles; its perbromide forms beautiful crystals.

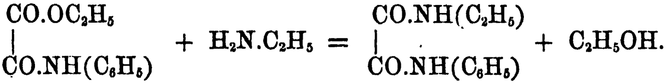
Derivatives of Dimethyloxamide, by O. Wallach and A. Boehringer.—Methylamine is most conveniently prepared by reducing chloropicrin with tin and hydrochloric acid; its aqueous solution acts easily on oxalic ether, and yields dimethyloxamide, which is readily soluble in water and alcohol, and crystallises in needles, subliming at 100°. Phosphorus pentachloride converts it into *chloroxalmethyline*, $C_4H_5ClN_2$, which is obtained in a pure state by distilling off the phosphorus oxychloride, dissolving the residue in cold water, adding potash and shaking with chloroform. The crude base which remains on volatilising the chloroform is distilled over baryta and thus obtained as a colourless liquid boiling at 204—205°. It is miscible with water in any proportion, has a strongly alkaline reaction, and yields with dilute sulphuric acid a solution, showing a fine fluorescence. It has an unpleasant, sweetish smell, and a caustic bitter taste. $C_4H_5ClN_2.HCl + H_2O$ is very soluble in water and alcohol, and forms oblique prisms, which are stable in the air, lose their water over sulphuric acid, and become then deliquescent.

$(C_4H_5ClN_2.HCl)_2PtCl_4$ crystallises from water or dilute alcohol in long reddish-yellow needles, which are almost insoluble in absolute alcohol. $C_4H_5ClN_2.C_2O_4H_2$ is much less soluble than the corresponding chloroxalethyline salt, and crystallises from alcohol in prisms. The picrate forms small yellow needles. The base gives precipitates with metallic salts.

$C_4H_5ClN_2.CH_3I$ crystallises from alcohol in white needles, and yields a periodide forming deep-red needles, and a perbromide crystallising in yellow plates.

Ethyl- and Methyloxamethane and Methylethyloxamide, by O. Wallach and P. West.—When dry ethylamine is passed into ethyl oxalate, an oily liquid is formed besides diethyloxamide; the former, which consists of *ethyloxamethane* $CO(OC_2H_5)—CO.NH(C_2H_5)$ is best obtained by allowing a solution of ethylamine in absolute alcohol mixed with ethyl oxalate to stand for some hours, and then distilling off the alcohol. The residue yields, on fractional distillation, first diethyloxamide and then a mixture of this body with ethyloxamethane. In order to separate these, the portion boiling between 240—250° is cooled down by a freezing mixture, and the diethyloxamide which separates out, is removed by means of a filter-pump. On rectifying the liquid, the pure compound is obtained as a colourless liquid boiling at 244—246°, which when pure has only a faint smell, but generally smells like the isonitrils. It is easily decomposed by water and more quickly by alkalis, with formation of ethyloxamic acid. On shaking it with milk of lime and evaporating the filtrate, $[CO.NH(C_2H_5)—CO.O]_2Ca + 2H_2O$ is obtained in well developed prisms; $[CO.NH(C_2H_5)—CO.O]_2Ba + H_2O$ does not crystallise so well. The free acid forms small flexible needles melting at about 120°. The formation of ethyloxamethane explains why Heintz, on separating the ethyl-bases by Hofmann's method, obtained ethyloxamic acid, and why it is so very difficult to obtain pure diethylamine.

Ethyloxamethane yields with aqueous ammonia a bulky precipitate of *monethyloxamide* $CO(NH_2)—CO.NH(C_2H_5)$, which is readily soluble in ether, hot alcohol, and hot water, and forms needles melting at about 202—203°, but subliming below this temperature. On heating it with aniline it yields *ethylphenyloxamide*, $CO.NH(C_6H_5)—CO.NH(C_2H_5)$, which is more conveniently prepared by adding an aqueous solution of ethylamine to an alcoholic of phenyloxamethane:



$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CO.NH(C_6H_5) \end{array} + H_2N.C_2H_5 = \begin{array}{l} CO.NH(C_2H_5) \\ | \\ CO.NH(C_6H_5) \end{array} + C_2H_5OH.$$

It forms needles, which resemble asbestos, melt at 169—170°, are almost insoluble in cold water, and dissolve but sparingly in hot water.

By the action of methylamine on ethyloxamethane, *methylethyloxamide* is formed, which very readily sublimes and melts at 155—157°.

When ethyl oxalate is treated with an alcoholic solution of methylamine, *methyloxamethane* is formed, which, as it solidifies at 8—10°, must be separated from the dimethyloxamide at the ordinary temperature by means of the filter-pump. It boils at 242—243°, and is easily decomposed by water and alkalis. The *methyloxamic acid* thus formed resembles the ethyl-compound, volatilises with steam, can be easily sublimed and melts at about 140°.

$[CO.NH(CH_3)—CO.O]_2Ca$ forms needles resembling asbestos when crystallised from a hot solution, but from cold water it separates in prisms or plates containing three molecules of water.

Monomethyloxamide, $CO.NH_2—CO.NH(CH_3)$, is sparingly soluble in water, water and ether, and crystallises from hot dilute alcohol in microscopic needles, melting and subliming at about 227—229°.

Dimethyloxamide, which was prepared from the preceding compound, is identical with that formed by the action of methylamine on ethyl oxalate.

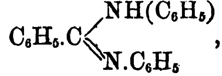
Methylphenyloxamide forms silky needles, which readily sublime and melt at 179—181°.

By the action of phosphorus pentachloride on methylethyloxamide, *chloroxalmethyline*, $C_5H_7ClN_2$, is obtained, which is separated in the same way as the corresponding methyl-derivative. It is a liquid boiling at 212—213°. Its hydrochloride crystallises in prisms containing water. $(C_5H_7ClN_2.HCl)_2PtCl_4$ crystallises from dilute alcohol in large compact plates. $C_5H_7.ClN_2.CH_3I$ forms white needles and a periodide crystallising in dark plates. The base gives, like its homologues, precipitates with metallic salts; $C_5H_7ClN_2.NO_3Ag$ is a crystalline precipitate.

When ethyloxamethane is added drop by drop to a mixture of phosphorus pentachloride and petroleum-naphtha, a quiet reaction takes place, which must be quickened by frequent shaking. On surrounding the resulting liquid with a freezing mixture, large prisms of $CO.OC_2H_5—CCl_2(NH)C_2H_5$ crystallise out, melting a little above 50°, and decomposing above 100°. C. S.

Action of Phosphorus Pentachloride on Benzanilide, Acetanilide and Acetethylamine.

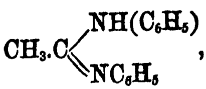
By O. WALLACH and M. HOFFMANN.—On heating gently equal numbers of molecules of benzanilide and phosphorus pentachloride, a liquid is obtained, depositing crystals on cooling. To obtain them pure, the phosphorus oxychloride was distilled off *in vacuo*, and the crystalline residue recrystallised from petroleum-naphtha. The compound thus produced, $C_6H_5—CCl{=}NC_6H_5$, forms large, glistening, transparent plates, which melt at 39—40°, and in contact with the air, change gradually into benzanilide. According to Gerhardt, who prepared this body, it is decomposed by heat into benzonitril and chlorobenzene, but the authors find that it distils without decomposition at about 310°. An excess of aniline converts it into $N_2(C_7H_5)(C_6H_5)_2H$, which has also been described by Gerhardt, who states that if the chlorine-compound is in excess, a compound having the composition of salicylic acid was produced, which the authors could not confirm. The former compound, also obtained by Hofmann, who called it benzyldiphenyldiamine, and by Limpricht, has the constitution



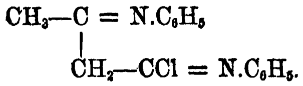
$$C_6H_5.C\begin{cases}NH(C_6H_5)\\N.C_6H_5\end{cases}$$

, and may be called *benzenyldiphenylamimide*.

Perfectly pure and dry acetanilide melts at 112—113°, and distils at 293°; hot dilute hydrochloric acid dissolves it without decomposition, but the concentrated acid resolves it in the cold into aniline and acetic acid. Phosphorus pentachloride acts readily on it, and, on using equal numbers of molecules, a liquid is formed, which at a low temperature yields crystals consisting probably of $CH_3.CCl_2.NH(C_6H_5)$. This body is very unstable and soon changes into a blood-red mass of $CH_5CCl = NC_6H_5$. Water converts it into acetanilide, and the solution contains two bases, which are not formed by the action of water, but are already contained in the crude product.

When aniline is added to the dry chloro-product a violent reaction takes place, and a hard mass is obtained which is soluble in water. On adding an alkali the base  $CH_3.C\begin{cases}NH(C_6H_5)\\NC_6H_5\end{cases}$, which Hofmann called *ethenyldiphenyldiamine*, is precipitated.

When the original chloro-product is heated above 50° a reaction sets in, which must be moderated by rapid cooling. The red syrup thus formed dissolves in water and gives with alkalis a precipitate consisting of oily drops which soon solidify. This compound is much more easily obtained by gently heating the liquid obtained by the action of phosphorus pentachloride on acetanilide until the red syrup is obtained, which is then quickly cooled and poured into ice-water. The liquid is well stirred up, and, after a few hours, filtered off from some resin and acetanilide. On adding ammonia to the filtrate the base, $C_{16}H_{15}ClN_2$, is obtained as a crystalline precipitate. It crystallises from petroleum-naphtha in small, glistening prisms, melting at 116—117°. Its salts do not crystallise well or form syrups; $(C_{16}H_{15}ClN_2.HCl)_2PtCl_4$ is a crystalline precipitate, which is soluble in hot water, and crystallises from hot alcoholic hydrochloric acid in large red crystals. The base has probably the following constitution:—



$$\begin{array}{l}CH_3—C = N.C_6H_5\\ \quad\ \ |\\ \quad\ CH_2—CCl = N.C_6H_5.\end{array}$$

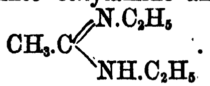
On boiling it with alcohol, it is converted into acetanilide, and on heating one molecule with two molecules of aniline it is resolved into ethenyldiphenylamidine and its hydrochloride:

$$C_{16}H_{15}ClN_2 + 2C_6H_7N = C_{14}H_{14}N_2 + C_{14}H_{14}N_2.HCl.$$

When the base is carefully heated in shallow vessels until it begins to redden at one point, and the flame is removed, the reaction proceeds through the whole mass, and on cooling a transparent, red mass is obtained which is the hydrochloride of a base not containing chlorine. This salt is readily soluble, and from its aqueous solution acetanilide crystallises out on standing. The free base is an amorphous precipitate, which is decomposed by heat. The platinochloride is very sparingly soluble in water, and could not be obtained quite pure. The base has probably the composition $C_{16}H_{14}N_2$.

Acetethylamine boiling at 205° acts violently on phosphorus pentachloride, and must therefore be added very gradually. The oxychloride and trichloride of phosphorus which are formed were removed by distillation *in vacuo*, and a syrup was left behind consisting of the hydrochloride of a base which was dissolved in a little water and precipitated with platinic chloride. The precipitate crystallises from hot dilute alcohol in large, yellowish-red monoclinic prisms, having the formula $(C_8H_{15}ClN_2.HCl)_2PtCl_4$. The free base suffers decomposition on separating it from its hydrochloride by an alkali. By shaking it out with chloroform, removing the latter and distilling the base with caustic potash, a liquid is obtained containing ethylamine and the base

$C_6H_{14}N_2$. which is a limpid, oily liquid boiling at 165—168°, soluble in water, and having an alkaline odour and reaction. Its aqueous solution precipitates the salts of the heavy metals. When boiled with aqueous potash it is resolved into ethylamine and acetic acid; it is therefore *ethenyldiethylamidine*,



$$CH_3.C\Big\langle\begin{matrix}N.C_2H_5\\NH.C_2H_5\end{matrix}.$$

C. S.

Selenureas and a Method of Estimating the Selenium in them. By P. SPICA (*Gazzetta chimica italiana*, vii, 90—99).—The starting point for the preparation of this new class of bodies, the selenureas, containing selenium in the place of the oxygen of ordinary urea, is potassium selenocyanate, which was obtained by Crookes' modification of Berzelius's method.

Monobenzylselenurea, $NH_2.CSe.NH(C_6H_5.CH_2)$.—This urea is formed on mixing aqueous solutions of benzylamine hydrochloride, and potassium selenocyanate, but it is better to operate with dry alcoholic solutions containing equal molecules of the two compounds, and after removing the potassium chloride, to evaporate the solution at first at a gentle heat and finally in a vacuum. The urea forms colourless crystals which melt at 70° with partial decomposition. It is very soluble in alcohol, ether, and water, and is very alterable, undergoing decomposition at the ordinary temperature, whether in the crystalline state or in solution. Nitric, sulphuric, hydrochloric, and acetic acids added to its solution cause a precipitation of selenium.

Isodibenzylselenurea, $NH_2.CSe.N(C_6H_5.CH_2)_2$, is prepared by mixing and heating hot concentrated aqueous solutions containing equal molecular weights of potassium selenocyanate and dibenzylamine hydrochloride. On cooling, the urea is deposited in the crystalline state, but somewhat impure from partial decomposition of the compound. It is better, as in the case of the monobenzyl derivative, to employ alcoholic solutions. This urea forms long, slender, colourless prisms, which are easily soluble in alcohol or ether, and also in hot water, but only slightly in the cold. Like the mono-derivative, it readily decomposes. Heated to 150° it begins to darken, and at 216° it decomposes with separation of a liquid.

The author has made numerous experiments with the selenocyanate analogous to those which are known to yield sulphureas when sulphocyanate is employed, but with indifferent success.

He concludes therefore that, owing to the instability of monophenylselenurea, of symmetrical diphenyl- and dibenzyl-selenurea, and of monotolyl- and symmetrical ditolyl-selenurea, he has not yet been able to realize the conditions under which they may be isolated, although indications of their existence in solution have been obtained.

Method of estimating the Selenium.—It was found that Carius's method of heating with concentrated nitric acid, and then precipitating the selenic acid as baric salt, gave very unsatisfactory results, as did also fusion with a mixture of sodium carbonate and potassium nitrate and precipitating as plumbic selenate. These ureas are, however, completely decomposed by concentrated hydrochloric acid, so that it is only necessary to add hydrochloric acid to an aqueous solution of a known weight of the urea, boil for a few minutes, leave the liquid to cool, and then collect, wash, and dry the selenium. The decomposition which takes place with the isodibenzyl urea gives rise to hydrocyanic acid and dibenzylamine hydrochloride—

$$NH\ CSe.N(C_7H_7)_2 + HCl = NH(C_7H_7)_2.HCl + CNH + Se.$$

C. E. G.

Ladenburg's Benzene Formula. By J. H. VAN'T HOFF (*Deut. Chem. Ges. Ber.*, x, 1881—1883).—The same difficulties beset the prismatic as the hexagonal formulæ of the aromatic compounds, and on the whole Kekulé's hexagon is simpler and better adapted to explain facts than Ladenburg's prism.
G. T. A.

Ammonium Compounds. By VICTOR MEYER (*Deut. Chem. Ges. Ber.*, x, 309—315).—The author and Lecco had previously shown that the substances synthetically obtained from ethyldimethylamine and ethyl chloride, and from triethylamine and methyl chloride are absolutely identical, exhibiting the same properties and reactions and giving rise to the same derivatives. On the other hand, Ladenburg and Struve have stated that the substances prepared from benzyl iodide and triethylamine and from ethyl iodide and benzyldiethylamine are not identical but only isomeric, although closely alike in most of their properties, *e.g.*, the melting point, appearance of the picrate and periodide, &c.: the former breaks up, according to these chemists, into benzyl iodide and hydriodide of triethylamine on boiling with hydriodic acid or evaporation on the water-bath, whilst the latter does not so decompose. On repeating these observations, however, the author concludes that this difference does not in fact exist, and that the substances prepared in these two ways are absolutely identical.

Benzyldiethylamine was prepared by heating in a sealed tube on the water-bath for a short time a mixture of equal numbers of molecules of pure diethylamine and pure benzyl chloride; the crystalline contents of the tube were dissolved in dilute sulphuric acid and the solution shaken with ether to remove traces of benzyl chloride; after heating to remove the dissolved ether soda was added, and the precipitated oil distilled fractionally to remove adherent diethylamine; the pure benzyldiethylamine boiled at 211—212° (corrected). Ladenburg and Struve prepared their base by acting on benzylamine with ethyl iodide. On heating in a sealed tube equivalent quantities of this benzyldiethylamine and ethyl iodide, a crystalline product was obtained constituting, when pure, colourless transparent prisms of extraordinary size and beauty, and readily soluble in water; neither on evaporation on the waterbath, nor on heating with aqueous hydriodic acid, did this body evolve benzyl iodide, but on heating it alone to a distilling temperature, benzyl iodide was eliminated to some extent.

By heating gently in a sealed tube a mixture of benzyl iodide (prepared from benzylchloride and potassium iodide) and triethylamine absolutely the same substance was obtained, no tendency whatever to split up with evolution of benzyl iodide on heating with aqueous hydriodic acid, being noticeable, although this body is evolved on dry distillation. The same result was obtained with the benzyltriethyl ammonium iodide prepared by uniting benzyl chloride to triethylamine, treating the product with silver hydrate, and converting the ammonium hydrate thus formed into iodide by hydriodic acid, this being the process employed by Ladenburg and Struve. A periodide was formed from each of these three samples by atmospheric oxidation.

It hence results that the observations of Ladenburg and Struve, as to the difference between the benzyltriethylammonium iodide formed in these two ways are erroneous. The error is not improbably due to the presence in the benzylamine of dibenzylamine; for the author finds that a mixture of benzyl iodide and benzyldiethylamine gives rise to dibenzyldiethylammonium iodide, which is decomposed by boiling with aqueous hydriodic acid, evolving benzyliodide and forming an oily distillate. The fourth "atomicity" of nitrogen in ammonium is therefore not different in function from the three in ammonia.

Lossen has recently stated that dimethyldiethyl-ammonium picrate becomes black before it melts, and hence that the melting point cannot be accurately determined. The author finds that the salt recrystallised after precipitation forms large diamond-like prisms, which do not change in the slightest degree on heating to 285°, when they completely melt. Decomposition does not ensue until fusion has taken place.

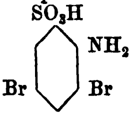
C. R. A. W.

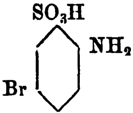
On the Replacement of Bromine and Sulphonyl by Hydrogen in the Benzenesulphonic Acids, and on the Orthobenzenesulphonic Acids. By H. Limpricht (*Deut. Chem. Ges. Ber.*, x, 315—321).—Brominated amidosulphonic acids of the benzene family are converted into amidosulphonic acids by heating them with hydriodic acid and phosphorus, but the reaction is so energetic that the intermediate stages cannot be discriminated; hydrobromic acid also fails to give satisfactory results, but hydrochloric acid answers well; thus by heating *tribromamido-benzenesulphonic acid*, $C_6H\left\{\begin{matrix}Br_3\\NH_2\\SO_3H\end{matrix}\right.$, to 140—160° in sealed tubes for 5 hours with hydrochloric acid and amorphous phosphorus, there are successively formed the di- and monobromamidosulphonic acids, and finally the amidosulphonic acid itself:

$$C_6H_2\left\{\begin{matrix}Br_2\\NH_2\\SO_3H\end{matrix}\right.,\quad C_6H_3\left\{\begin{matrix}Br\\NH_2\\SO_3H\end{matrix}\right.,\ \text{and}\ C_6H_4\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right..$$

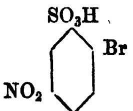
Benzenesulphonic acids are decomposed by heating with hydrochloric acid, the SO_3H group being replaced by H. The ease with which this action takes place varies much with the acid; thus, some acids are quickly decomposed at 140—150°; others require several hours at this temperature; with others higher temperatures are requisite, and some withstand several hours' heating to 250°. As a rule the more highly substituted benzenes are most readily decomposed: a certain amount of bye-product is generally also formed; thus with brominated nitrobenzenesulphonic acids yellow vapours become visible in the heated tube.

On treating benzenesulphonic acids with nitric acid, the SO_3H group is replaced by NO_2; in many cases, however, further nitration also ensues simultaneously.

The mother-liquors of metanitrobenzenesulphonate of calcium furnish on deoxidation a mixture of three isomeric acids, viz., *ortho-*, *meta-*, and *paramidobenzenesulphonic acids;* one of these (the meta-acid) crystallises in fine needles, and can be removed by cautious washing with cold water. On heating the remaining mixture of gritty crystals to 100°, the para-acid becomes anhydrous and the crystals fall to powder, so that the ortho-acid can be separated by merely sifting and recrystallising two or three times the small lumps thus separated. On treatment with bromine, orthoamidobenzenesulphonic acid forms *dibromamidobenzenesulphonic acid* of structure 

and with smaller quantities of bromine the *monobromamidobenzenesulphonic acid* 

this latter was converted into diazo-compound, and thence by means of hydrobromic acid into a *dibrombenzenesulphonic acid* melting at 71°, in which the two bromines are in the para position with reference to one-another. This acid yields a well-crystallised chloride: hence this monobromamidobenzenesulphonic acid is identical with that examined by Thomas (*Deut. Chem. Ges. Ber.*, ix, 1866); it crystallises with 1 molecule of water.

Orthobrombenzenesulphonic acid is readily obtained by converting the orthoamido-acid into a diazo-compound, and boiling with hydrobromic acid; it yields a well-crystallised chloride melting at 51° (not oily and non-crystalline as formerly described); on treatment with nitric acid two *nitrobromobenzenesulphonic acids* are formed, one only in small quantity yielding an anhydrous barium salt crystallising in small plates, a chloride melting at 97°, and an amide fusing at 215° and forming well-crystallised salts, the other possessing the structure 

.
This acid forms a barium salt crystallising in needles; the acid crystallises with 2 molecules of water and loses this water at 130—135°, fusing whilst so doing. The ammonium, potassium, sodium, and silver salts are anhydrous; the lead and barium salts crystallise with $5H_2O$; the calcium salt with $4H_2O$, and the zinc salt with $7H_2O$; the chloride melts at 92° and the amide at 205°. By reduction with tin and hydrochloric acid, *amidobrombenzenesulphonic acid* is formed, crystallising in difficultly soluble needles with $2H_2O$; on treatment with hydriodic acid and phosphorus, this acid yields *metamidobenzenesulphonic acid;* and by treatment of its diazo-derivative with hydrobromic acid, it forms paradibrombenzenesulphonic acid, from which two reactions its structure is known.

Orthochlorobenzenesulphonic acid was similarly prepared from the diazo-derivative. This acid, like the corresponding orthobrombenzenesulphonic acid just described, yields a chloride which can be readily crystallised. Hitherto this body has been described as oily; it melts at 28·5° and forms an amide melting at 188°.

Orthoiodobenzenesulphonic acid was also prepared from the diazo derivative by treatment with hydriodic acid; the chloride of this acid melts at 51°, the amide at 170°; the barium salt is anhydrous, the potassium salt crystallises with H_2O.

The melting points of the chlorides and amides of the orthobenzenesulphonic acids are—

	Chloride.	Amide.
Orthonitrobenzene-sulphonic acid	67·	183
Orthochloro „ „	28·5	183
Orthobromo „ „	51·	186
Orthoiodo „ „	51·	170

C. R. A. W.

Benzoyl-compounds of Orthoparamidophenol. By K. Stuckenberg (*Deut. Chem. Ges. Ber.*, x, 380—381).—The hydrochloride of α-diamidophenol is readily obtained by reducing 1 part of α-dinitrophenol with 4 parts of tin and 12 of hydrochloric acid, and adding to the solution concentrated hydrochloric acid, which precipitates the salt almost free from tin in compact needles. On boiling it with benzoyl chloride, it yields the two following compounds :—

Dibenzoyl-α-diamidophenol is freely soluble in alcohol, chloroform, glacial acetic acid and aniline, more sparingly in benzene, and very sparingly in ether, and forms dark or reddish little prisms.

Tribenzoyl-α-diamidophenol is insoluble in alcohol, ether, benzene, and chloroform, sparingly soluble in glacial acetic acid, and forms microscopic crystals melting at 231—233°. Cold concentrated nitric acid converts it into a nitro-compound, crystallising from acetic acid in yellow needles. C. S.

Action of Nitric Acid on Tribromophloroglucin. By R. Benedikt (*Liebig's Annalen*, clxxxiv, 255—260). *Tribromodinitropropionic Acid.*—Tribromophloroglucin dissolves in concentrated nitric acid, and, after standing, a white crystalline body separates out. When pure this substance forms white, glittering, odourless plates, which are insoluble in water and acids, but soluble in alcohol and ether. They have the formula $C_3HBr_3N_2O_6$. By the prolonged action of water, this compound is converted into bromopicrin and oxalic acid, with evolution of nitrous oxide. When reduced with sodium-amalgam, it yields methylamine together with oxalic and hydrocyanic acids. These results indicate that the substance in question is tribromodinitropropionic acid, CBr_3—$C(NO_2)_2$—COOH. E. N.

Brazilin. By C. Liebermann and O. Burg (*Deut. Chem. Ges. Ber.*, x, 1883—1888).—*Tetracetobrazilin.* When brazilin is treated with anhydrous acetic acid at 130°, a body is obtained which when purified by recrystallisation from alcohol, consists of fine white needles having a satiny lustre, melting at 149—151°. The crystals are anhydrous and have the composition $C_{16}H_{10}(C_2H_3O)_4O_6$.

Brazilin and Lead.—An aqueous solution of brazilin gives with sugar of lead a white precipitate, which on filtering and drying becomes of a rosy colour. Its composition is $C_{16}H_{12}PbO_5 + H_2O$. The water is given off at 130°, and the substance becomes darker in colour.

Brazilein.—A solution of brazilin becomes cherry-red when an alkali is added to it in presence of air. A salt of the colouring matter, brazilein, is formed, which becomes of a violet colour on addition of acids, and of a fine gold colour when dry. It is amorphous, but not anhydrous. Its composition at 130° is $C_{16}H_{12}O_5$. Crystallised brazilein may, however, be obtained by treating a hot aqueous solution of brazilin with an alcoholic solution of iodine. The crystals consist of grey, silvery, rhombic plates; they dissolve in alkalis with a purple-red colour, but the brazilein is precipitated from the solution by acids.

Chloro- and Bromobrazilin.—Obtained by treating aqueous solutions of brazilin with chlorine- and bromine-water. Their composition is $C_{16}H_{12}Cl_2O_5$ and $C_{16}H_{12}Br_2O_5$. The above experiments show that the formula $C_{16}H_{14}O_5$ is at least highly probable for brazilin: and, if so, hæmatoxylin, $C_{16}H_{12}O_6$, is simply brazilin in a higher state of oxidation, and these bodies stand in the same relation to each other as alizarin and purpurin. G. T. A.

On some Derivatives of Deoxybenzoïn. By A. Zagoumenny (*Liebig's Annalen*, clxxxiv, 163—174).—When deoxybenzoïn and an alcoholic solution of potassium hydrate are heated in a sealed tube to 150°, stilbene hydrate and the potassium salt derived from diethylcarbobenzonic acid are formed. Diethylcarbobenzonic acid, $H.C_{18}H_{17}O_2$, crystallises in white needles, soluble in alcohol and ether, and yields a white soluble sodium salt and a white, amorphous, sparingly soluble silver salt. By the action of an ethereal solution of ethyl iodide, the dry silver salt is converted into ethyl diethylcarbobenzonic acid, $C_2H_5.C_{18}H_{17}O_2$, a heavy oily liquid. Nitric acid dissolves diethylcarbobenzonic acid with a transient red coloration, and on addition of water dinitrodiethylcarbobenzonic acid, $H.C_{18}H_{15}(NO_2)_2O_2$, separates out as a white flocculent precipitate. On crystallisation from hot alcohol it yields white needles melting at 155—156°, and soluble in 26 parts of boiling alcohol. By fusion with excess of alkali, potassium diethylcarbobenzonic acid is split up into potassium diethylbenzoate and potassium benzoate.

By heating to 150° in a sealed tube, a mixture of deoxybenzoïn and a solution of potassium hydrate in normal propyl alcohol, there is formed stilbene hydrate and the potassium salt derived from a new acid. The new acid crystallises partially in long slender plates and partially in heavy octohedrons, both having the formula $C_{20}H_{22}O_2$, corresponding with dipropylcarbobenzonic acid. The octohedral crystals melt at 90°, and are easily soluble in alcohol and ether, whilst the slender plates are less soluble in these media, and fuse at 139°. The latter yield with nitric acid rhombic plates, melting at 176° and soluble in 40 parts of boiling alcohol, and having the composition of dinitro-dipropylcarbobenzonic acid, $H.C_{20}H_{19}(NO_2)_2O_2$. The octohedral crystals yield on nitration a resinous body easily soluble in alcohol. Pseudopropyl alcohol does not decompose deoxybenzoïn in the same manner as the normal alcohol.

A mixture of dioxybenzoïn and solution of potassium hydrate in isobutyl alcohol, on being heated to near 140°, yields stilbene hydrate and the potassium salt of diisobutylcarbobenzoic acid. This acid, $C_{22}H_{25}O_2.H$, crystallises in rhombic tables, melting at 148°, and soluble in 20 parts of boiling alcohol. If the isobutyl alcohol is replaced by amyl alcohol, *diamylcarbobenzonic acid*, $H.C_{24}H_{27}O_2$, is formed, which crystallises in slender needles, soluble in 28 parts of boiling alcohol.

E. N.

On the Pharmacological Group of Piperine. By R. BUCHHEIM (*N. Rep. Pharm.*, xxv, 335—344).—The sharp-tasting substance in pepper is not piperine, as supposed by Oerstedt in 1819, for it was found by Pelletier in 1821, that the purer the piperine, the less sharp was its taste. The substance to which pepper owes its sharpness was isolated as follows:—The alcoholic extract of pepper does not contain the acrid principle; the portion insoluble in water and in alcohol, shaken with ether, left scarcely anything but piperine in a slightly impure state. The ether dissolves in acid resin and chlorophyll. It was shaken with potash, and the ether was removed by distillation. The residue was deep yellow, and was dissolved in alcohol and treated with animal charcoal. This residue is rather more soluble in ether than piperine, and was separated from the base by repeated solution in a very small quantity of ether. It formed a yellowish-brown mass, as viscid as thick turpentine, and had a very strong taste of pepper. It amounted to two-thirds of the weight of the piperine. It was boiled with potassium hydrate to convert the small quantity of piperine into piperic acid. On addition of sulphuric acid, piperidine sulphate was formed. The small residue of fatty acids was removed by agitation with light petroleum. The yellow resinous residue could not be obtained in crystals.

The resin, therefore, is converted into piperidine by treatment with alcoholic potash. The author has named it *chavicine*. As piperine on treatment with alcoholic potash yields piperidine and piperic acid, so chavicine gives piperine and chavicic acid, which differs from piperic acid by its not crystallising, and by its ready solubility in alcohol. It is hardly attacked by bichrome and sulphuric acid.

From the *Radix Pyrethri*, a plant used as a spice, from its resemblance to pepper, a substance somewhat similar to chavicine was extracted by a process similar to that given above. It crystallised in small, fatty needles from its solution in petroleum when allowed to stand for a long time *in vacuo*. The author named it *pyrethrine*. It is insoluble in water, and in dilute acids or alkalis, but dissolves in alcohol, ether, and carbon disulphide. On treatment with alcoholic potash it splits up into piperidine, and an acid closely resembling chavicic acid, named by the author *pyrethric acid*. It is not altered by sodium amalgam, nor is it easily oxidisable. With bichrome and sulphuric acid a slight smell of butyric acid was perceptible.

The cress, *Herba spilanthis*, was dried, exhausted with alcohol and then with ether, the latter solvent acquiring the hot taste peculiar to the plant. It was shaken with potash to remove chlorophyll, &c. The residue, after the ether had been distilled off, was of a greenish-brown colour, and soluble in alcohol, a viscid fat containing chlorophyll remaining undissolved. The residue on evaporation of the alcohol had the properties of pyrerythrine, but was too impure to admit of a careful comparison. With alcoholic potash it decomposed into piperidine and a substance apparently identical with pyrerythric acid. The cress, accordingly, contains the same sharp-tasted constituent as the *Radix Pyrethri*.

By action of benzoyl chloride on piperine, Cahours obtained a substance named by him benzopiperide. It has the formula $C_5H_{10}.N.C_7H_5O$; he also, by a similar process, prepared cymyl piperide $C_5H_{10}.N.C_{10}H_{15}O$. There are, therefore, five substances known, derivatives of piperidine, in which one atom of hydrogen is replaced by an acid radicle, viz., piperine, chavicine, pyrerythrine, benzopiperide, and cumyl piperide, all of which on treatment with alcoholic potash, yield piperidine and a salt of the respective acid. The physiological action of piperidine presents no striking peculiarity, and resembles that of a salt of ammonia or ethylamine. None of the above-mentioned acids have any violent action. Their compounds with piperidine, however, which, as they do not form salts, probably are bodies resembling amides, have all a violent action on the organism. They are crystalline, and soluble in alcohol, when the acids from which they are derived are crystalline and soluble in alcohol. The compounds of piperidine with alcohol-radicles found by Cahours, viz., methyl-, ethyl-, and amyl-piperidine, have no resemblance to piperine in their physiological effects. The action of piperine on the organism is simply that of an inflammatory agent, and an irritant of the sensory nerves. W. R.

On the Pharmalogical Group of Atropine. By R. BUCHHEIM (*N. Rep. Pharm.*, xxv, 344—358).—As atropine, when treated with baryta-water, decomposes into tropic acid, $C_9H_{10}O_3$, and tropine, $C_8H_{15}NO$, it may be viewed as tropine in which the only replaceable atom of hydrogen is replaced by the radicle of tropic acid, thus: $C_8H_{14}O.N.C_9H_9O_2$. In crude atropine a second base exists of the formula $C_{18}H_{25}NO_4$, called by Hübschmann *belladonnine*. The author obtained a quantity of crude belladonnine, prepared by precipitating atropine sulphate with potassium carbonate till the precipitate was no longer resinous, but a powder. From this syrupy dark-brown mass the belladonnine was precipitated by ammonia, well washed with water to remove brown colouring matter, and one-half was neutralised with sulphuric acid and added to the rest. From this mixture ether, or better, chloroform extracted pure belladonnine, leaving atropine and some belladonnine as sulphate. One-half of this residue was thrown down with ammonia, then added to the other half, and shaken with ether. The aqueous residue, on addition of ammonia, gave first a precipitate of belladonnine and then of atropine. The belladonnine, separated from its solution in ether, was dried; it was a yellowish-brown resin, almost insoluble in water, easily soluble in alcohol and in chloroform, and somewhat less in ether. It forms neutral salts with acids, the sulphate being a resin.

With alcoholic potash it decomposed into tropine and a resinous body, named by the author *belladonnic acid*, which differs in its properties from tropic acid. Belladonnine may therefore be regarded as a compound of this acid with tropine.

Tropine, obtained by distilling the residues from which the belladonnine had been separated with lime, is a liquid of the consistence of castor-oil, but after some time becomes crystalline. It is easily soluble in water and in alcohol, has a smell resembling that of tobacco, and a strong alkaline reaction. Its sulphate is easily soluble.

Benzoyl-tropine, prepared by adding benzoyl chloride to tropine, closely resembles atropine, which is tropyl-tropine.

Physiological experiments with these bodies showed that tropine has no action on the pupil, unless an atom of hydrogen is replaced by an acid radicle, but that this action depends on the nature of the radicle. Atropine possesses it more strongly than belladonnine, or benzoyl-tropine. The exhibitory action also on the heart is recognisable in tropine, but to a less degree than when the hydrogen is replaced.

It is probable, from Geiger and Hesse's experiments, that the alkaloïd obtained from the seed of the datura, called by them *daturine*, is a substituted tropine, the acid probably being an isomeride of tropic acid.

The same chemists isolated an alkaloïd from henbane, and named it hyoscyamine, which, according to Höhn and Reichardt's experiments, is decomposed by baryta-water into hyoscinic acid, $C_9H_{10}O_3$, and hyoscine, $C_6H_{13}N$; the two formulæ when added together amount to that of hyoscyamine, $C_{15}H_{23}NO_3$. Either, then, the formula of the acid or of hyoscine, or of the alkaloïd must be incorrect, as no water is evolved. The action of hyoscyamine is similar to that of atropine. Two samples of hyoscyamine were obtained by the author: one was crystallised, and acted physiologically as stated by Hellmann; the other was a syrup, and produced a reflex action of the nerves, which was not observable with the crystallised alkaloïd; the probability is, therefore, that a second alkaloïd was present. For this hypothetical substance, the author suggests the name *sikeranine*, from Sikerân, the Persian name of Hyoscyamus. W. R.

Investigations on the Alkaloïds of the Fly Agaric. By E. HARNACK (*Chem. Centr.*, 1876, 560).—After the discovery of muscarine in this fungus by Schmiedeberg, he noticed that other alkaloïds were contained in the crude muscarine, one of which, amanitine, is best separated by the following process. The hydrochlorides of muscarine and amanitine are squeezed between folds of bibulous paper. The former is more deliquescent and soaks into the filter-paper, while the latter remains. This process is repeated till the salts are separated. To obtain pure muscarine, advantage is taken of the greater solubility of muscarine aurochloride in water.

The residue left after extraction of muscarine from fly agaric, has no poisonous action. It has no poisonous effect on flies, so that the fly-poison of the agaric must be destroyed when allowed to dry.

Amanitine aurochloride has the formula $C_6H_{14}NOCl.AuCl_3$, and is probably identical with choline, though muscarine, the formula of which is the same as that of betaine or oxyneurine, is not the same as the latter. By the action of hydriodic acid, the iodine being subsequently removed with silver carbonate, an inactive neutral body, resembling a base, is formed, the formula of the aurochloride of which is $C_2H_{15}NO_3Cl.AuCl_3$. It is therefore more highly oxidised, and contains more carbon than amanitine and muscarine. W. R.

Synthesis of Muscarine and allied Ammonium Bases. By O. SCHMIEDEBERG and E. HARNACK (*Chem. Centr.* 1876, 554—560).—From former investigations by Harnack, muscarine aurochloride was found to have the formula $C_5H_{14}NO_2Cl.AuCl_3$, so that muscarine is an isomeride of betaine, except in the number of atoms of hydrogen. Muscarine, when heated, evolves trimethylamine; like betaine it differs from choline by containing an atom of oxygen more. It has been stated that betaine can be prepared from choline by oxidation with nitric acid; the authors have proved that choline prepared from hen's eggs yields muscarine on oxidation with strong nitric acid, and they have demonstrated the identity of the bases known as choline, neurine, sincaline, and amanitine (prepared from fly agaric) with artificial choline prepared from ethene-chlorhydrin and trimethylamine. No other base was obtained by decomposing lecithin, but for some time doubt was entertained of the identity of the choline from lecithin with that obtained from other sources, on account of the peculiar appearance of its platinum salt, arising from impurities.

The choline chloride, when oxidised to muscarine, should be as dry as possible, and must be warmed on the water-bath with strong nitric acid. After red fumes cease to be evolved, more nitric acid must be added, and heat applied with a flame. The oxidation product is dissolved in alcohol, and precipitated with platinic chloride. The platinic chloride is purified by recrystallisation from alcohol, and the unchanged choline chloride is again treated with nitric acid. It is more advantageous to oxidise the choline platinochloride, and separate the unchanged salt from the resulting muscarine platinochloride by taking advantage of the greater solubility of the former. There is, nevertheless, a great loss of substance, owing chiefly to the action of the nitrous fumes.

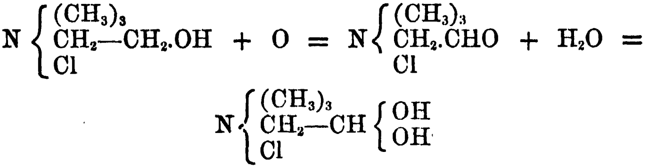
If dilute nitric acid be used, a nitro-compound of the formula $(C_4H_{10}N_2O_3Cl)_2.PtCl_4.2H_2O$ is formed. Betaine was not observed as a product of oxidation of choline.

Muscarine platinochloride crystallises in small octohedrons. Its formula is $(C_6H_{14}NOCl)_2.PtCl_4.2H_2O$. The chloride is prepared from this salt by evaporating it with excess of potassium chloride, and extracting it with alcohol and chloroform; if sulphuretted hydrogen be used to precipitate the platinum, the muscarine is reduced to choline. Muscarine hydrochloride separates from its solution in chloroform in large colourless crystals, and frequently in groups of needles or prisms, which do not effloresce over sulphuric acid, and deliquesce easily on exposure to air.

The *hydroxide*, $N\begin{cases}(CH_3)_3\\C_2H_5O_2\\OH\end{cases}$, is prepared from the chloride with moist silver oxide. It is a crystalline caustic mass.

It is beyond doubt that muscarine from this source is identical with that prepared from fly agaric. On distillation with lead oxide trimethylamine was evolved. The gold salt of muscarine yielded gold equivalent to 3·12 p.c. of hydrogen in the muscarine, showing that the formula of the chloride is probably $C_6H_{14}NO_2Cl$, and not $C_5H_{12}NO_2Cl$, which contains only 2·63 p.c. of hydrogen.

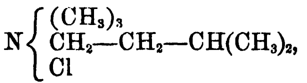
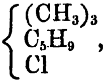
The relation of muscarine to betaine is probably the same as that of chloral hydrate to trichloracetic acid, and the reaction expressing the oxidation of the choline is probably this:—



$$N\left\{\begin{array}{l}(CH_3)_3\\ CH_2—CH_2.OH\\ Cl\end{array}\right. + O = N\left\{\begin{array}{l}(CH_3)_3\\ CH_2.CHO\\ Cl\end{array}\right. + H_2O =$$

$$N\left\{\begin{array}{l}(CH_3)_3\\ CH_2—CH\left\{\begin{array}{l}OH\\ OH\end{array}\right.\\ Cl\end{array}\right.$$

In muscarine, however, as in chloral hydrate, two atoms of hydrogen cannot be replaced by an acid radicle, but other compounds are formed. It was thought probable that the position of the atoms of oxygen might have some connection with the poisonous properties of muscarine. It happens, however, that compounds of trimethylammonium bases are also poisonous in an analogous manner to muscarine.

Isoamyltrimethylammonium chloride,  $N\left\{\begin{array}{l}(CH_3)_3\\ CH_2—CH_2—CH(CH_3)_2\\ Cl\end{array}\right.$, is obtained by the action of aqueous trimethylamine on amyl bromide at 100°. The platinochloride crystallises from water in thin hexagonal tables. The valeryl compound,  $N\left\{\begin{array}{l}(CH_3)_3\\ C_5H_9\\ Cl\end{array}\right.$, prepared in the same manner with amylene bromide, forms a platinochloride, crystallising in yellow semiglobular aggregations of crystals, and an aurochloride, in thin irregular, sparingly soluble plates. The chloride forms a syrupy mass, easily soluble in water, alcohol, and chloroform, which slowly becomes crystalline on standing over sulphuric acid. Both bases are very poisonous, a few milligrams being a sufficient dose to kill a cat when injected subcutaneously, with phenomena similar to those of muscarine poisoning. The pupil, however, does not contract. With frogs the pulsation of the heart ceases, but can be re-induced by application of atropine. At least 1 mgr. of the chloride is necessary, whereas $\frac{1}{30}$ to $\frac{1}{40}$ mgr. of muscarine produces the same effect.

W. R.

Relation between Asparagin and Proteïn. By R. SACHSSE (*Chem. Centr.*, 1876, 584—585).—Since Pfeiffer's investigation, it has appeared probable that proteïn is convertible into asparagin, and *vice versâ*. The author tries to show that this conversion is comparable with one which has long been known. Pfeiffer gives the following table, showing the manner in which 100 grams of asparagin is changed into 125·5 grams of legumin with 16·77 p.c. of nitrogen:—

	Legumin.	Asparagin.	Difference.
C........	64·9	36·4	+ 28·5
H	8·8	6·1	+ 2·7
N	21·2	21·2	0
O	30·6	36·4	– 5·8

There is no analogy for any process by which hydrogen and carbon are absorbed and oxygen evolved. It is more probable that a substance containing less hydrogen is formed from asparagin. The author, therefore, imagines a substance having the formula $C_4H_4N_2O$, and expresses the conversion of legumin into that substance, thus:—

	Legumin.	$C_4H_4N_2O$.	Difference.
C	64·9	36·4	+ 28·5
H	8·8	3·0	+ 5·8
N	21·2	21·2	0
O	30·6	12·1	+ 18·5

The numbers of the difference represent approximately the formula $C_{2\cdot5}H_5O$. It is, therefore, possible to express the formation of proteïn from asparagin by the equation—

$$x(C_4H_6N_2O_3) - 2xH_2O + xC_{2\cdot5}H_5O = \text{Proteïn.}$$

The substance, $C_{2\cdot5}H_5O$, has the formula of an aldehyde of the fatty series, $C_nH_{2n}O$, and might express a mixture of such aldehydes if the data were more trustworthy. But there are other facts which support the theory that proteïn is formed by union of an aldehyde with asparagin minus water. The compound, $C_4H_4N_2O$, is the nitril of malic acid; now, the nitril of formic acid, viz., hydrocyanic acid, combines with aldehydes to form alanine, leucine, &c. In a similar manner, the nitril of malic acid may combine with aldehydes to form proteïn, the aldehydes originating from the oxidation of the carbohydrates.

W. R.

Proteïn Crystalloïds from Bertholletia excelsa. By R. SACCHSE (*Chem. Centr.*, 1876, p. 583—584).—The grains of proteïn-like bodies were washed out of the para-nut, with salad-oil, in the same way as starch with water. The residue was freed from fat by ether, and dried. From 300 grams of the bruised kernels, the author obtained 30—40 grams of dry proteïn-like bodies, containing 9·27 p.c. of nitrogen. This preparation was contaminated with the remains of cells; for purification, it was kneaded with alcohol and squeezed through fine linen; the first portions which came through were found to contain about 12 p.c., of nitrogen. After being dried at 110°, it appeared under the microscope, to be free from cells. 12 to 15 p.c. of nitrogen represent 66 to 69 p.c. of proteïn-substance; the ash constitutes 14 p.c.; the remainder, 17 to 20 p.c., consists, probably, of organic acids and carbohydrates, for its solution, when heated for a short time, reduces alkaline cupric hydrate. The crystalloïds may be prepared from the proteïn by digesting the latter in water at 40—50°

filtering and maintaining the filtrate for some time at that temperature; the crystalloïds then deposit on the sides and bottom of the vessel; they are then washed with cold water. They may also be separated by passing carbonic anhydride into the solution of the proteïn. From 20 grams of substance, 5 grams of the crystalloïds were obtained. When examined under the microscope, they are seen consist of thin scales. They show signs of double refraction. The mean of five analyses shows them to have the composition—

C.	H.	N.	O.	P_2O_5.	S.
51·00	7·25	18·06	21·51	0·82	1·36

They belong, therefore, to the class of caseins from plants, the nearest analogue being conglutin, which contains the same percentage of nitrogen, but differs in containing less sulphur. W. R.

Some Constituents of Coto-barks. By JUL. JOBST and O. HESSE (*Deut. Chem. Ges. Ber.*, x, 249—254).—Coto-bark yields, by exhaustion with ether, a brown, resinous mass, which crystallises after a time, and consists, for the most part, of paracotoïn, oxyleucotin, and leucotin. These bodies may be separated by fractional crystallisation from hot alcohol.

Paracotoïn, $C_{19}H_{12}O_6$, forms small yellow laminæ, easily soluble in chloroform, ether, and boiling alcohol, sparingly in petroleum and boiling water. The aqueous solution deposits it in nearly colourless laminæ. It is neutral and tasteless; insoluble in ammonia, and nearly so in potash- and soda-ley; soluble in strong sulphuric and nitric acids, forming yellow solutions. It melts at 182° to a yellow liquid, which crystallises on cooling. At a higher temperature, it sublimes in brilliant yellow laminæ. Baryta-water converts it into *paracotoic acid*, according to the equation—

$$C_{19}H_{12}O_6 + H_2O = C_{19}H_{14}O_7.$$

Paracotoic acid forms an amorphous yellow powder. It is easily soluble in ether and alcohol, and is left as an amorphous residue on evaporating the latter solution. The same acid is produced on heating paracotoïn with weak potash-ley, accompanied, however, by a small quantity of other products, amongst which is the following:—

Paracumarhydrin, $C_9H_8O_3$, forms delicate white laminæ, melting at 85°, and dissolving easily in alcohol and ether, and sparingly in water.

Oxyleucotin, $C_{21}H_{20}O_7$, forms thick, heavy, white four-sided prisms, which melt at 133°. The fused substance solidifies in an amorphous mass on cooling. It dissolves easily in hot alcohol, chloroform, and ether, but not in water or alkalis. It is tasteless and neutral.

Leucotin, $C_{21}H_{20}O_6$, forms very delicate light white prisms, which melt at 97°, and dissolve very easily in alcohol and ether. It occurs in large quantity in coto-bark.

The alcoholic mother-liquor of the foregoing substances leaves, on evaporation, a brown resin, which gives up to very weak potash-ley the following body:—

Hydrocotoïn, $C_{22}H_{20}O_6$, crystallises from alcohol in brilliant pale-yellow prisms, and from boiling water in delicate white needles. It is neutral and tasteless, melts at 98°, and solidifies in a crystalline mass. It dissolves in alkalis, and is precipitated from the solutions by acids, even by carbonic acid. J. R.

Safrol. By A. ARZRUNI (*N. Rep. Pharm.*, xxv, 615—622).—Safrol is the solid substance obtained by exposing sassafras oil to a considerable degree of cold. The crystals melt between 8·5° and 10°, the substance may be kept in the liquid state for some time at a temperature considerably lower than that of the melting point. Safrol is unchanged in the air.

The crystals belong to the monoclinic system: the relations of the axes are—

$$a : b : c = 0{\cdot}31658 : 1 : 0{\cdot}57832,$$

the inclination of a to $b = \beta = 111° \, 59\tfrac{1}{2}'$. M. M. P. M.

Physiological Chemistry.

Differences of Chemical Structure and of Digestion amongst Animals. By F. HOPPE-SEYLER (*Pflüger's Archiv. f. Physiologie*, xiv, 395—401).—In the glands of the stomach of every warm-blooded animal a ferment is found, named *pepsin*, which when extracted with water containing 0·2 per cent. of hydrochloric acid, gives a solution, capable, at the temperature of the blood, of rapidly dissolving albumin.

A somewhat similar ferment, discovered by Fick and Murisier in the stomachs of frogs, pikes and trout, differs from pepsin by acting most actively at a low temperature, as at 20°, and losing its digestive power at the temperature of the blood. This difference in the action of the two ferments probably resembles that between the diastase of the pancreas and of germinating barley.

In carnivorous plants, the acid reaction of the secretions, and the formation of peptone, coupled with the results of Gorup-Besanez's investigations on *Nepenthes*, suggested that the digestive property of these secretions is due to a ferment similar to pepsin. But experiments made in conjunction with Dr. E. Herter on *Drosera rotundifolia*, have shown that it is neither pepsin, nor identical with the ferment contained in the stomachs of cold-blooded vertebrata.

It would be well to find out whether the so-called "spittle" of *Doleum galea*, which, according to Boedeker and others, contains free sulphuric and hydrochloric acids, also contains a ferment and is used for digestion.

Having sought in vain to find any statements as to the digestive ferments of invertebrata, I examined the river cray-fish.

In the stomach is found a plentiful supply of a yellowish-brown, feebly acid juice, which possesses an energetic fermenting power, and rapidly dissolves fibrin. The addition of a few drops of a ·2 per cent. hydrochloric acid solution stops the action, and other experiments show the ferment to be similar to, if not identical with, the albumin-dissolving ferment of the pancreas of vertebrata. The aggregated tubular glands, commonly known as the liver, proved to be the source of this juice. These glands may therefore be looked upon as forming the pancreas.

In the river cray-fish a proper stomachic digestion, such as is peculiar to the vertebrata, is entirely wanting, and consequently they possess enormously large glands having the property of the pancreas.

Comparative anatomists have called these glands liver, without however having enquired whether they performed the function of that organ or not. In vertebrata their function is the formation of bile and glycogen. Though a small quantity of the latter was found, it might easily have resulted from the large amoeboïd cells present in the organ. The constituents of bile were, however, not present, and so far as I know, neither biliary colouring matter nor acids have ever been found in any invertebrate. On the other hand, no vertebrate is known which, possessing a liver, does not form bilirubin, biliverdin and biliary acids. Now the biliary colouring matter is due to the decomposition of the colouring matter of the blood; but, with few exceptions, hæmoglobin is not found in the invertebrata, and those which do possess it in their blood, lack red corpuscles, the hæmoglobin being merely dissolved in the plasma. A liver producing biliary acids and colouring matter may consequently be considered as characteristic of vertebrata, just as well as a closed circulatory system containing blood with red corpuscles.

It is strange that amphioxus should be classed among the vertebrata, simply from the relative position of the spinal chord and digestive cavity to the *chorda dorsalis*, while with the exception of the latter, it possesses nothing in common with the vertebrata. A sound system of classification should not only consider the morphology, but summarise the entire organisation. Considered generally, the cephalopoda stand next to the vertebrata; amphioxus is lower in the scale.

Again, comparing the constituents of tissues of lower organisms with those of higher, one finds first the appearance of mucin-forming tissue, soon chondrin-forming, and lastly, in the cephalopoda the appearance of glutin-forming tissue. The same order is found in the successive stages of development of the embryo, and this can scarcely be considered an accidental agreement.

Looking at the question broadly, we find that the chemical composition of the tissues and the chemical functions of the organs present undoubted relations to the stages of development, which show themselves in the zoological system, as well as in the early stages of development of each individual higher organism. These relations deserve further notice and investigation, and are qualified in many respects to prevent and correct errors in the classification of animals.

It is generally supposed that the study of development is a purely morphological science, but it also presents a large field for chemical research.

F. J. L.

Formation of Glycogen in the Bodies of Animals. By J. FORSTER (*N. Rep. Pharm.*, xxv, 733—739).—Sugar was injected into the veins of dogs which had been kept without food for several days, the animals were killed, and the glycogen in the liver was estimated. Comparable experiments, omitting the injection of sugar, were also performed. A notable increase in the amount of glycogen found followed the injection of sugar. The author regarded this increase as a product of the increased decomposition of albuminous bodies in the organism brought about by the sugar. Sugar was detected in considerable quantities in the blood of the animals experimented upon.

M. M. P. M.

Dissemination of Glycogen in the Animal Organism. By ABELES (*Chem. Centr.*, 1876, 230).—In adult animals the presence of glycogen has been demonstrated in very few localities, except in the liver and in the transversely striated muscles. The author has found that the normal spleen, as well as the lungs and kidneys of dogs, fed for three days on bread, contains glycogen. He proposes to extend his researches on the subject.

W. R.

Formation and Separation of Pepsin. By P. GRÜTZNER (*Chem. Centr.*, 1876, 38).—Pepsin diminishes during digestion. The author contradicts Schiff's statement that certain substances, dextrin for example, are capable of causing an increase in the quantity of pepsin in the juices of the stomach. Schiff's method of determining pepsin in the stomach is declared to be untrustworthy. The author's researches upon the variation in the amount of pepsin under different physiological conditions, show that the amount of pepsin in the stomach does undergo variation; that the smaller cells of the stomach or pylorus (Hauptzellen) when large and clear, contain much pepsin; when small and turbid, little pepsin. The amount of pepsin increases from the moment that nourishment is administered (to dogs) until the expiration of 9 hours; it then decreases until the expiry of 30 hours, when it again very slowly increases till 40 hours are passed, after which it remains constant.

The administration of common salt causes a larger secretion of pepsin: the salt appears to act by decomposing a compound containing pepsin in the pylorus.

M. M. P. M.

The Pancreatic Juice of Herbivora. By A. HENRY and P. WALLHEIM (*Pflüger's Archiv. f. Physiologie*, xiv, 457 to 468).—It appears probable that the pancreatic juice of the rabbit, unlike that of the dog, continues to flow during fasting, though to a lesser extent than during digestion. The quantity secreted amounts to from 0·6—0·7 c.c. per hour, and gives, as the mean of 14 experiments, 1·76 per cent. of solid constituents. The pancreatic juice of the sheep contains from 2 to 3·5 per cent. of solid constituents.

Chemically and physically these secretions differ considerably from that of the dog. Unlike the latter, the juice of the rabbit does not solidify on warming, but flocculent masses separate out from it and rise to the surface. Where the secretion shows on boiling but a slight opalescence, it becomes quite cloudy if acidified before boiling; the precipitate, however, re-dissolves in excess of strong acid. The juice dropped into dilute acetic acid, liberates carbonic acid. Nitric acid produces a flocculent precipitate, turning yellow on warming. Alcohol precipitates an albuminate.

The secretion of the sheep acts as above, except that on dropping it into dilute acetic acid, a precipitate is formed which immediately redissolves.

The juices operated upon are believed, and, so far as possible, proved to be, the normal secretions of the organ. F. J. L.

On Sulphocyanates in Urine. By R. Gscheidlen (*Pflüger's Archiv. f. Physiologie*, xiv, 401—412).—The sulphates and phosphates having been removed from 100 c.c. of urine by baryta-water, the filtrate evaporated to a syrup, extracted with alcohol, and the residue left on evaporating this extract dissolved in water, a solution is obtained which after decolorisation with charcoal strikes a deep red colour with ferric chloride. This colour is due to the presence of a sulphocyanate. The absence of such other substances as could produce it having first been proved, the presence of a sulphocyanate was fully verified.

Experiments were made on the reactions of this substance, and, unless there be another body present, the results which have been obtained show that the various reactions observed by Schönbein, Sertoli, Lobisch and Voit are due to the presence of this sulphocyanate. This statement must be modified if, as sometimes stated, hyposulphurous acid is to be found in urine.

The results of 14 experiments made by means of Oehl's volumetric method gave 0·0225 as the quantity of sulphocyanogen in 1000 parts of urine; this corresponds with 0·0314 of sodium sulphocyanate and 0·0376 of potassic sulphocyanate.

The question now arose whether it was due to the saliva or formed by some special organ. The saliva of a dog having been diverted from the mouth was collected separately, and the urine also collected during six days. The saliva contained sulphocyanates, the urine none. A similar experiment in which the urine was collected for nine days gave a like result.

The total quantity of sulphocyanates in the saliva, as estimated by Oehl, agrees with that found in the urine.

From these investigations it appears that a sulphocyanate is a normal constituent of the healthy urine of mammals. F. J. L.

Relation of Phosphoric Acid to Nitrogen in Urine. By W. Zülzer (*Chem. Centr.*, 1876, 567).—The author finds that the amount of phosphoric acid emitted in urine does not, as is generally supposed, bear a constant proportion to the nitrogen. From his own and others' researches, it appears that in the case of dogs and cats fed on pure flesh, the relation of nitrogen to phosphoric acid is, on the average, 100 : 10·4—12·8. With addition of fat to the diet, 100 : 9·2—11·9. When the animal is fed on flesh, after previous starvation, 100 : 6·6—9·6; with potatoes, the phosphoric acid is

2·5—29·7 per cent. of the nitrogen; with bread, 21·6—29·7 per cent.; with potatoes and fat, 30·8—37·3 per cent.; with calves' brains, 21·7 per cent. After abstinence from food, the proportion of phosphoric acid decreases for 1 or 2 days, and then gradually rises for 6 to 11 days, again slightly decreases, as in the case of a diet of animal food. Shortly before death, the amount again increases. With man, the usual proportion is 17—20 per cent. In the forenoon the ratio is higher than in the afternoon or night. Children have a much greater proportion than older people. The greatest observed amount was 58·5 per cent., and the smallest, 8·7 per cent. In old age, the phosphoric acid increases slightly. After reference to the proportion in cases of disease, the author comes to the conclusion that the variation of proportion is related to the change of matter in the nerves, and that in general, the change of material of the flesh depends on the nervous activity. W. R.

Separation of Sal-ammoniac in Urine. By C. VOIT (*N. Rep. Pharm.*, xxv, 727—733).—A known quantity of sal-ammoniac was administered to a dog which had fasted for some days. The amount of urea found in the urine increased considerably; nevertheless experiment showed that the greater part of the ammonia originally administered as sal-ammoniac passed through the body unchanged. The increase in secretion of urea cannot therefore be traced to the synthesis of that compound from the sal-ammoniac administered. The author is disposed to regard the action of sal-ammoniac as comparable with that of sodium chloride, viz., as promoting decomposition of albuminoïd substances in the organism. M. M. P. M.

Influence of Cold on the Curdling of Milk. (*Dingl. polyt. J.*, ccxxiii, 329).—By preserving milk in ice-water at 1° to 2° for some time, it remains perfectly sweet and unaltered for 14 days, as stated by Soxhlet (*Wien. Landw. Zeitung*, 1876, 264). After 17 days it began to taste slightly sour, the rancid taste increasing, until after 28 days the milk was curdled when boiled. After 34 days it curdled in ice-water. Considerable quantities of volatile fatty acids had been formed by oxidation of the milk-fat in the air. This formation of acids is quite different from the formation of lactic acid, which takes place by decomposition of milk-sugar, by means of an organised ferment at a higher temperature, but is retarded by the low temperature of Swartz's method, whereas the oxidation is not prevented by cold. D. B.

The Poison of the Cobra de Capello. By A. W. BLYTH (*Analyst.*, i, 204—207).—The poison, which may be obtained by pressing the parotid glands, while the fangs are erected, over a watch-glass, is an amber-coloured, syrupy, frothy liquid, of spec. grav. 1·046, and of feeble acid reaction, drying rapidly on exposure to air, leaving a yellow, acrid, pungent powder, to the amount of about 33 per cent. The poison contains albumin, a minute quantity of fat, and 1·4—1·5 per cent. of ash, mainly consisting of sodium chloride, is obtained on incineration; it is not decomposed at 100°, and the uncoagulated portion preserves its activity for a long time. On heating the yellow powder to 270°, it blackens, and above 270° a sublimate is formed. A similar substance, crystallising in needles, may be obtained by dialysing the poison. It exists in the venom to the amount of 10 per cent., and is highly poisonous, appearing to be the only active principle. It is obtained pure by means of the lead-salt, and evaporation in a vacuum. For want of material no analyses have been made, but the name of *cobric acid* is proposed for it. A dilute solution of potash, or a weak alkaline solution of potassium permanganate destroys the poisonous properties of cobra poison. E. W. P.

Notes on some peculiar Modifications of Animal Fats, the result of Fermentation and Digestion of the Neutral Fats of Food prior to and during Assimilation. By H. C. BARTLETT (*Analyst.*, 175).—The analysis of a large number of pancreatic glands, taken from pigs, dogs, calves, and other animals, showed that the fatty components of most of the glands contain a considerable proportion of volatile fatty acids combined with glycerin. These are, perhaps, not true synthetical reproductions of the glycerides, but compounds of soluble fatty acids and glycerin, resulting from the decomposition of the natural saponification-product during digestion; they are almost identical with the similar compounds separated from butter by the means now in use for analysing butter. In order to estimate the proportion of volatile oil in the fat extracted from these glands, the author uses potash and alcohol for saponification, and decomposes with dilute acid (sulphuric or hydrochloric). This being accomplished in a retort, the condenser is luted tight, and the aqueous liquid distilled over until an exact fourth is left, to which fresh water is added, and the distillation continued as long as the water condensed gives any acid reaction. Baryta-water is added to the distillate, and the whole redistilled down to about 5 per cent. of its original bulk, after which it is evaporated to dryness in a vacuum at 45°. The barium salts thus obtained are in triplicate, one series being easily soluble, the intermediate salts less so, and the third somewhat difficult of solution. Since the author has not yet succeeded in separating these salts, each in sufficient purity from the others, he cannot speak with certainty as to their exact identity with the caprates, butyrates, caprylates, and caproates of butter; but he can confirm the presence of caproic acid, caprates, and caprylates by the crystalline form and other appearances of these salts. It is further stated that a considerable quantity of volatile and soluble fatty matter may be found during the digestion of fat in the intestine, and particularly at the time of absorption. From this the author was induced to conclude that the transformation of a portion of neutral fats into fatty acids and glycerin by the pancreatic and other digestive fluids, is the result of fermentation. D. B.

Chemistry of Vegetable Physiology and Agriculture.

Researches on Chlorophyll, and its relation to the Colouring Matter of Blood. By L. LIEBERMANN (*Chem. Centr.*, 1876, 615).—Chlorophyll obtained from various plants has, optically at least, the same properties, and appears to be a compound formed from *chlorophyllic* acid, and a basic compound, called by the author, *phyllochromogen*, neither of which has been completely isolated, although the acid can in part be separated pure. The base appears to be the substance which, under the influence of oxidising and reducing agents, assumes various colours. The author's grounds for making this statement are:—1. That the colouring matter, which becomes green on reduction, exhibits those absorption-bands, which should remain after the separation of chlorophyllic acid. 2. That undecomposed chlorophyll and chlorophyllic acid do not show such changes of colour. 3. That, according to the researches of Fremy and Kromayer, chlorophyll is affected by reducing or oxidising agents, only when partial separation takes place, a blue substance being the result.

The formation of the colouring matter of the flower from leaf-green may be represented as a decomposition of the chlorophyll, by the action of an acid or a ferment, into its acid and basic constituents, the latter being converted by oxidation into the violet-blue, or red colouring matter of the flower. The formation of the colouring matter of faded leaves cannot be compared with that of the colouring matter of flowers; the fading is not due to any great change in the chlorophyll, but is merely a reduction without splitting up. Chlorophyll and phyllochromogen exhibit certain analogies to the colouring matter of the blood. 1. Their absorption spectrum is similar to that of oxyhæmoglobin oxidised by potassium permanganate. 2. With oxidising or reducing agents, they react like hydrobilirubin, bilirubin, bilicyanin, biliverdin. 3. Chlorophyll is said by many to contain iron. 4. Chlorophyll, like hæmatin, is dichroïc in alcoholic or alkaline solutions. 5. Chlorophyll has been found to act as an animal pigment, having been detected by Pocklington in cantharides. E. W. P.

On the Function of Chlorophyll. By R. SACHHSE (*Chem. Centr.*, 1876, 550—552).—Since Bäyer discovered that furfurol, when mixed with resorcin or pyrogallol, gives with a trace of hydrochloric acid, a beautiful indigo-blue substance, and surmised its identity, or at least analogy with chlorophyll, the author has repeated Bäyer's experiments, with the following results. Pyrogallol is dissolved in alcohol; hydrochloric acid and ferric chloride are added, and finally some furfurol. The fluid slowly turns green, and keeps its colour for a long time, finally, however, turning brown, with a tinge of violet. The absorption-spectrum of this colour shows a tolerably well defined band in the red, while blue and violet are almost wholly absorbed, the band being nearly coincident with the line 1 of chlorophyll. It has been supposed that the function of chlorophyll in plants was to absorb light, and convert it into vital force. But the unabsorbed light, viz., yellow, is most energetic in decomposing carbonic anhydride; besides chlorophyll is continually being formed and destroyed. Several theories have been advanced on this subject. Wiesner supposes chlorophyll to be the active agent in reducing carbonic anhydride, and attempted to reduce that substance by passing a current through a solution of chlorophyll in alcohol.

Kraus supposes a body, which he calls leucophyll, to combine with aldehydes, which are reduction-products of carbonic acid. This compound is continually destroyed, and leucophyll again formed, when the reaction again takes place. Timiriaseff's hypothesis is that a substance, called by him *chlorophyllin*, is changed by light into a brownish-yellow body, *phylloxanthin*, oxygen being evolved, and replaced by carbonic oxide formed by reduction of carbonic anhydride, and the colour being restored. The author of this paper believes that chlorophyll is the first product of the reduction of carbonic anhydride and water, and is itself converted by further change and reduction into starch and carbohydrates. This accounts for the circumstance that when starch is in course of formation, the amount of chlorophyll diminishes. Wiesner also draws attention to the fact that in young *Orabanchaceæ*, starch is converted into chlorophyll as the plant grows older. Hoppe has recently shown that pyrocatechin is a derivative of carbohydrates, and furfurol has long been known to be connected with them.

The author's views stand in opposition to Wiesner's experiments, which tend to show that chlorophyll in alcoholic solution is destroyed by light and oxygen, but he maintains that this may not express the reaction which occurs in the living plant, for almost all colours may be destroyed by bleaching, and the colour of chlorophyll is also destroyed by reduction. The synthetical aim is, therefore, to convert chlorophyll into carbohydrates. Should this be accomplished, we shall be better able to understand the formation of these substances from their elements. W. R.

Absorption of Water and Lime Salts by the Leaves of Phaseolus multiflorus. By J. Boehm (*Landw. Versuchs. Stat.*, xx, 51—59).—Primordial leaves of *Phaseolus multiflorus* can often be dried to a fourth, or even a fifth of their original weight, without entirely losing the power of producing and decomposing carbonic acid when placed in an atmosphere of pure hydrogen. The leaves, even when dried to about half their original weight, will recover their freshness if immersed, with the exception of the stems, in water. Leaves that have been thus revived, dry on exposure to the air much more quickly than freshly cut ones.

Phaseolus multiflorus seedlings, the roots of which have been carefully wrapped in damp cloths, but the leaves suffered to dry by exposure to the air, until each has not more than half its former weight, do not revive when placed underneath a bell-jar, with their roots immersed in water. They revive completely, however, when immersed, with the exception of the roots; when, therefore, a certain point is reached, the water necessary for their recovery can be taken up by the leaves only, and not by the roots. If a seedling be cut so that only the two primordial leaves remain upon the stem, and one of these be dipped beneath the surface of water whilst the other is kept exposed to the air, the leaf out of the water will remain quite fresh; but if both leaves be allowed to dry to a certain extent before the one is immersed, the other will not again revive.

Seedlings of *Phaseolus multiflorus* possess the property of absorbing through their leaves not only water, but also the lime salts necessary for their development. Carbolic acid, in the proportion of 1 part per 1,000, can be added to the water used for their nourishment, without hindering growth. H. H. B. S.

Honey-dew. By H. HOFFMANN (*Landw. Versuchs. Stat.*, xx, 61). —That honey-dew is the production of aphides, or other insects is questioned by the author. He cites cases of two plants, one a *Camellia japonica*, and the other an ivy, both of which, though absolutely free from aphides, were found covered with this substance. In the case of the camellia no insects of any kind could be discovered upon the plant.

H. H. B. S.

Analyses of Plants. By A. H. CHURCH (*Journal of Botany*, March, 1876; *Arch. Pharm.* [3], x, 60—65).—*Lactuca sativa.*—The fresh and well-developed leaves were experimented on. They were first dried in warm air, afterwards at 100°, and a portion of the dried substance was burnt. The ashes were analysed and proved to be very rich in nitrates. The albuminous matter was determined in a portion of the dried leaves, after removal of all nitrogenous substances (nitrates and salts of ammonia), by means of a hot solution of carbolic acid. Analysis gave the following numbers:—Water 95·98 p. c., albuminous matter 0·71, starch, sugar, gum 1·68, cellulose and lignose 0·52, chlorophyll and fat 0·22, ash 0·89; total, 100·00.

Chondrus crispus.—Various statements have been made regarding the presence of sulphur-compounds in the so-called *Irish pearl moss* (*carragheen*). The author found that this plant contained a large quantity of sulphur which was mostly present as sulphate. The carefully purified and powdered alga was oxidized by means of nitric acid and potassium chlorate and the sulphuric acid precipitated with a barium salt. No less than 6·41 p. c. of sulphur was obtained, while the ash contained only 2·64 p. c. 100 parts gave 18·78 water, 9·38 albuminous matter, 55·54 gelatinous matter, &c., 2·15 cellulose and 14·15 ash.

Nasturtium officinale.—The investigation of this plant afforded further proof of the fact that water and marsh plants possess the capability of assimilating large quantities of mineral substances. It contained in the fresh state only 0·082 p. c. of sulphur, equal to 1·195 on the dry plant. The ethereal oil which it yields on distillation is rich in nitrogen but free from sulphur. 100 parts of the plant contain 93·11 water, 1·50 albuminous matter, 2·92 starch, sugar, and gum, 0·66 cellulose and lignose, 0·53 chlorophyll and fat, and 1·28 ash.

Fagus sylvatica.—A large quantity of the brown scales (*perulæ*) of the leaf-buds of the common beech were collected, with the view of ascertaining the degree in which the more valuable elements of nutrition—phosphorus, nitrogen, potassium—are thrown out by the tree in the form of these bud-scales. The scales contained 15·36 p. c. of moisture and yielded on drying 7·70 p. c. of ash. The burnt substances, amounting to 92·30 p. c., contained 0·59 p. c. nitrogen. 100 parts by weight of dry substance gave 91·71 carbon, hydrogen, and oxygen, 0·59 nitrogen, 0·41 potash, 0·22 phosphoric acid, 0·17 sulphuric acid, 0·43 silica, 6·47 lime and other ash constituents. Nitrogen, potash, and phosphoric acid gave a total of 1·22 p. c. on the dry scales—a result which agrees perfectly well with the nature of the function of these organs in the economy of the plant and with the time of their development. In their chemical composition, as well as in a physiological point of view, these scales are distinctly opposite to those portions of the plant which take part in the reproduction process.

Ulmus campestris.—The female flowers of the elm tree differ very much from the beech-scales as regards their contents of nitrogen, phosphorus, and potassium. They were collected immediately after their fall (22 May, 1875) and analysed after drying. They yielded 8·15 p. c. of ash, and the burnt part contained 3·31 parts of nitrogen. 100 parts by weight of dry substance gave 88·54 carbon, hydrogen, and oxygen, 3·31 nitrogen, 2·39 potash, 0·97 phosphoric acid, 1·34 sulphuric acid, 0·40 silica, and 3·05 lime and other ash-constituents.

Triticum sativum.—By moistening a grain of wheat with water and carefully stripping it, a thin skin is obtained which consists of three layers. The two outer layers have a greyish colour with irregular structure, while the inner layer is yellow and contains nitrogen. There is reason to believe that these three layers, which are combined firmly (and cannot be separated by mechanical means), form the pericarp of the caryopsis, and it is interesting to investigate the manner by which this pericarp in its chemical composition is distinguished from the testa and endopleura and also from the embryo. 100 parts by weight yielded—

	Pericarp.	Embryo.
Water	15·17	12·53
Fat	1·31	4·18
Albuminous substances	10·37	35·70
Cellulose and lignose	70·51	3·12
Starch, dextrin, &c.		38·71
Ash	2·64	5·76
	100·00	100·00

These results show how these two parts of the fruit vary in chemical composition. The amount of phosphoric acid in the ash is 15·3 p. c. in the pericarp and 60·58 p. c. in the embryo, a proportion which, although it may be expected, had nevertheless not yet been proved experimentally.

D. B.

Chemical Study of the Mistletoe (Viscum album). By H. GRANDEAU and A. BOUTON (*Compt. rend.*, lxxxiv, 129—131).

—The authors have compared the composition of the ash of the mistletoe with that of the ash of the branches of several trees on which it grows. The paper gives the analytical figures, and the general results are:—The composition of the stems of the mistletoe differs much from that of the branches on which the parasitic plant grows; it varies with the nature of the supporting tree, and has always much more potash and phosphoric acid than the latter, but much less lime. R. R.

Cocoa. By C. Heisch (*Analyst*, 1876, 142).—The results of the analyses are embodied in the following table:—

Examination of Roasted Bean after removal of Husk.

	Husk.	Fat.	Nitrogen.	Albuminoïd substances.	Ash.
Caracas	13·8	48·4	1·76	11·14	3·95
Trinidad......	15·5	49·4	1·76	11·14	2·80
Surinam......	15·5	54·4	1·76	11·14	2·35
Guayaquil	11·5	49·8	2·06	13·03	2·50
Grenada......	14·6	45·6	1·96	12·40	2·40
Bahia	9·6	50·3	1·17	7·40	2·60
Cuba	12·0	45·3	1·37	8·67	2·90
Para	8·5	54·0	2·00	12·66	3·05

	Ash soluble in water.	Ash soluble in HCl.	H_3PO_4 in ash.	Moisture.	Starch, gum, cellulose, &c.
Caracas	2·15	1·80	1·54	4·32	32·19
Trinidad....	0·90	1·90	0·93	3·84	32·82
Surinam....	0·80	1·85	1·23	3·76	28·35
Guayaquil ..	1·75	1·75	1·87	4·14	30·47
Grenada	0·60	1·80	1·35	3·90	35·70
Bahia	0·90	1·70	1·26	4·40	35·30
Cuba	0·95	1·95	1·13	3·72	39·41
Para	1·40	1·65	1·00	3·96	26·33

M. M. P. M.

Birch-sap. By O. Henner (*Analyst*, i, 179).—In March and April the sap of the common birch tree rises with extraordinary power and in great quantity, and escapes freely from any wound that may be inflicted on the tree. This juice, which in some parts of Germany is allowed to ferment, when it is said to yield an agreeable, mild, alcoholic beverage, has the following chemical composition:—Acidity, calculated as acetic acid = 0·0156; total solid residue = 1·8255, and mineral matter = 0·0646 p. c. The solid residue included 0·0176 N and 1·10 glucose, cane-sugar being entirely absent. The juice turns the plane of polarisation to the left, 0·2. The ash contains:—

Cl.	CO_2.	SiO_2. Soluble.	Insoluble.	H_2SO_4.	P_2O_5.	CaO.	MgO.
0·708	20·937	0·114	1·530	7·448	10·855	18·825	10·105

	Na_2O.	K_2O.		
	0·939	29·283	=	100·744
Minus O for chlorine......				0·158
				100·586

The tree from which the juice was collected grew on a slaty soil.

D. B.

Influence of Nitrogenous Manures on the yield of Alkaloïds in certain Plants. By J. Jobst (*Chem. Centr.*, 1876, 192).—Broughton showed that nitrogenous manures affect not only the absolute, but also the relative quantity of alkaloïds formed in the Cinchona plant; that further, the total quantity of alkaloïds in Cinchona species was from 20 to 50 p. c. higher in manured soils than in soils which were not manured; and that also the manured Cinchona plants varied considerably according to the form in which the nitrogen was applied. By using sulphate of ammonium the total quantity of alkaloïds in *Cinchona succirubra* showed an increase of 2·36 p. c., that of quinine only 0·67 p. c. Guano applied to the same species increased the yield to 0·53 p. c. and 0·13 p. c. Sulphate of ammonium increased the total quantity of alkaloïds in the *Cinchona officinalis* to 1·12 p. c., of quinine 0·57 p. c., while guano gave 2·53 p. c. and 2·01 p. c. The use of farmyard manure increased the total quantities to 2·81 and 4·75 p. c., while the quantities of cinchonidine and cinchonine were reduced in a corresponding degree.

The following numbers may serve to illustrate how profitably farmyard manures may be employed for raising the value of *Cinchona officinalis*:—

Analysis of the bark of *Cinchona officinalis* manured with sulphate of ammonium—

3·1 p. c. quinine at 270 m.	=	873 marks.
2·6 p. c. cinchonidine and cinchonine average value at 85 m.	=	221 „
Total per 100 kilos. of bark	=	1,058
With farmyard manure—		
7·1 p. c. quinine at 270 m.	=	1,917
0·3 p. c. cinchonidine and cinchonine at 85 m.	=	25
Total per 100 kilos. of bark	=	1,942 „

Meanwhile Dietrich investigated the behaviour between manures and the formation of alkaloïds in poppies, and arrived at the following results:—A very poor unmanured soil, which was almost free from nitrogen, gave an opium containing only ½ p. c. of morphine. Potash and phosphoric acid were unable to increase the quantity of the latter. Chili saltpetre raised it to 1½ to 2 p. c., while sulphate of ammonium gave as much as 6½ p. c.

By comparing the behaviour of sulphate of ammonium and of farmyard manures with the above and other experiments, the author concludes that the largest quantity of alkaloïds may be obtained from the latter. D. B.

Loss of Plant-nutrients through Rivers. (*Dingl. polyt. J.*, ccxxiii, 328; *Fühling's Landw. Zeitung*, 1876, 751).—Breitenlohner and Harlacher calculate that the river Elbe, which takes up all the Bohemian rivers, carries away only $\frac{1}{4}$ of the total precipitate, while in Bohemia $\frac{3}{4}$ of the water is lost by evaporation, percolation, &c. The water carried off by the Elbe, amounting to about 5 milliards of cubic meters per year, contains about 455,950 tons of suspended matter and 518,900 tons of dissolved substances. The following nutrients are present:—

	CaO.	MgO.	K_2O.	Na_2O.	$NaCl$.	H_2SO_4.	H_3PO_4.
	t.	t.	t.	t.	t.	t.	t.
Suspended	2,480	1,440	20,280	4,550	—	230	1,250
Dissolved.	114,500	22,000	25,150	28,450	21,100	37,850	—
Total	116,980	23,440	45,430	33,000	21,100	38,080	1,250

D. B.

The Fundamental Scientific Principles of Geognosy. By A. ORTH (*Landw. Versuchs-Stat.*, xx, 63—69).—The object of this paper is to draw attention to the importance of considering the order and nature of the different strata in order to form a correct opinion of a soil.

H. H. B. S.

Schizomyces-fermentation of Glycerin, Mannite, Starch, and Dextrin. By ALB. FITZ (*Deut. Chem. Ges. Ber.*, x, 276—283).—This is a continuation of a previous paper on the same subject, an abstract of which appeared in this Journal (1877, i, 226).

Glycerin.—When schizomyetes are sown in a fermentable liquid containing a large proportion (say 10 per cent.) of glycerin, rapid fermentation sets in after a day or two and ceases in about 14 days, though much of the glycerin still remains undecomposed. The mycelium of the fungus has then entirely disappeared, the sediment containing only inactive spores. If now the liquid be decanted and distilled to remove the butyl alcohol formed in the fermentation, and poured back upon the sediment, the spores vegetate and multiply afresh and rapid fermentation again sets in. Hence it is expedient to employ solutions containing not more than about 3 per cent. of glycerin. Fermentation being over, the liquid is to be decanted from the sediment, the butyl alcohol distilled off, the residue, after cooling, returned to the sediment, and about 3 per cent. of glycerin added, with enough water to make up the original volume. The accumulation of calcium butyrate and caproate which thus takes place does not affect the schizomyces.

Ammonium sulphate or phosphate may be substituted for pepsin in the fermentable liquid with good results. A liquid containing 150 parts of glycerin, 1·5 of potassium phosphate, 0·7 of magnesium sulphate, 6 of ammonium sulphate, and 30 of calcium carbonate, in 3,000 parts of water, was rapidly brought into fermentation by an infinitesimal quantity of schizomycetes, the alcohol thereby formed being chiefly normal butyl alcohol.

The yield of crude alcohols in the author's experiments was about 14 per cent. of the glycerin employed, a very small portion only boiling at a lower temperature than butyl alcohol. Other products of the fermentation of glycerin were caproic, butyric, and probably lactic acids, and a volatile base not yet examined.

Mannite.—A 5 per cent. solution of mannite containing either pepsin or ammonium sulphate yielded by fermentation with schizomyces normal butyl alcohol, ethyl alcohol, and succinic acid.

Starch.—A trace of schizomyces introduced into a liquid composed of 100 part of starch, 0·1 of potassium phosphate, 0·02 of magnesium sulphate, 1·6 of ammonium phosphate, 40 of chalk, and 3,000 of water set up fermentation in 24 hours. The products were a little alcohol, chiefly ethylic, and a large quantity of acid.

Dextrin yielded more alcohol than starch. J. R.

Nitrification by Organized Ferments. By T. Schloesing and A. Müntz (*Compt. rend.*, lxxxiv, 301—303).—A wide glass tube a meter in length was filled with 5 kilos. of quartz sand which had been heated to redness and 100 grams of powdered chalk. The mixture in the tube was watered every day with a fixed quantiy of sewage, which occupied eight days in passing to the bottom of the tube.

During the first twenty days there was no formation of nitric acid, but at the end of that it appeared, and increased rapidly in quantity until the water flowing from the lower end of the tube no longer contained a trace of ammonia. The lapse of twenty days before nitrification took place proved that it was not due to the action of the oxygen of the air on the ammonia. When the experiment had lasted four months, vapour of chloroform was sent through the tube, the formation of nitric acid ceased immediately, and recommenced only when fresh germs obtained from land possessed of marked nitrifying properties were sown in the sand.

It is thus shown that nitrification is caused by organized ferments; further, that a sandy and barren soil, if it contain sufficient lime to neutralize the nitric acid, may serve admirably for the purification of sewage. F. D. B.

Analytical Chemistry.

Gas Apparatus for Quantitative Blowpipe Analyses. By T. Hirschwald (*Chem. Centr.*, 1876, 359).—To the foot of an ordinary Bunsen burner is screwed a short upright tube for the blast, having a fine opening at the top; above is placed a jacket, having a side opening for the introduction of gas, and narrowed at a few millimeters above the opening of the blast-pipe; a carrier screwed on to the outer tube serves to hold a small furnace of coke or graphite, bored vertically, and allowing of the internal suspension of the crucible on a platinum ring, the whole being covered by a lid. Lead precipitates, &c., can be more easily heated in 2—3 minutes with such a vertical blowpipe, than with the ordinary ones in use. E. W. P.

On some Blowpipe Reactions. By E. J. CHAPMAN (*Chem. News*, xxxv, 36).—*Uselessness of Turner's Flux.*—Turner's flux, which consists of acid potassium sulphate and calcium fluoride, gives, when heated in the blowpipe flame with a borate, a momentary green coloration. With many borates it fails entirely, whereas with others it is useless, seeing that they tinge the flame green when heated alone.

Comportment of certain Alloys under the Action of the Blowpipe.—In examining these reactions, about equal portions of the metals (forming the alloy) may be placed together, on charcoal, and subjected to the action of a reducing flame.

1. *Platinum and tin* unite, with violent deflagration and emission of light, forming a hard, brittle, and infusible globule.

2. *Platinum, zinc, and tin* unite, with violent action, the zinc throwing off long flakes of oxide.

3. *Platinum and zinc, per se,* do not combine, the zinc burning into oxide.

4. *Platinum and lead* unite quietly, forming a brittle globule.

5. *Platinum and thallium* unite quietly; the resulting globule is dark externally, gray internally, and quite brittle.

6. *Platinum and bismuth* unite quietly, or with merely slight spitting, into a dark brittle globule.

7. *Platinum and copper* combine quietly, though not very readily, into a hard, light-coloured, malleable globule.

8. *Platinum and silver* unite quietly, but not very readily unless the silver be greatly in excess, into a white malleable globule.

9. *Platinum and gold* unite quietly, forming (if the gold be somewhat in excess) a yellow malleable globule.

10. *Gold and tin* unite quietly into a very brittle globule.

11. *Gold and zinc* do not combine *per se;* the zinc burns into oxide.

12. *Gold and lead* combine quietly, forming a grey brittle bead.

13. *Gold and thallium* unite quietly, but separate again to some extent during cooling. The globule may thus frequently be flattened out, but not without cracking at the sides. If the metals remain united, the button is dark blackish-grey, and quite brittle.

14. *Gold and bismuth* unite quietly and readily, forming a very brittle globule.

15. *Gold and copper,* and (16), *gold and silver,* unite, and form a malleable globule.

17. *Silver and tin* unite quietly into a malleable globule.

18. *Silver and lead* unite readily into a malleable globule.

19. *Silver and thallium* combine readily; globule, malleable.

20. *Silver and bismuth* unite readily and quietly; the globule is brittle, but admits of being slightly flattened out.

21. *Silver and copper,* and (22), *silver and gold,* form malleable globules. The gold alloy, even with gold largely in excess, is quite white. If it be flattened out, and heated in a platinum spoon with some bisulphate of potash, it will become yellow from the silver on the surface being dissolved. On re-melting the flattened disc, a silver-white globule is again obtained.

23. *Copper and tin* unite into a grey and partially malleable bead,

the surface of which, in the outer flame, becomes more or less thickly encrusted with cauliflower-like excrescences of oxide.

24. *Copper and zinc* do not quite fuse *per se* into a globule, the zinc burning into oxide. Under soda, or soda and borax, brass is readily formed.

25. *Copper and lead* form a dark-grey globule, which is sufficiently malleable to admit of being extended on the anvil.

26. *Copper and thallium* melt into a dark-grey malleable globule.

27. *Lead and tin* unite readily, but the globule immediately begins to oxidise, throwing out excrescences of white and yellow oxide. On removal from the flame, it still continues in ignition, and pushes out further excrescences. The unoxidised internal portion (if any remain) is malleable.

28. *Lead and bismuth* unite readily; the molten globule acquires a thin dark coating of oxide on the surface only, and admits of being flattened out more or less upon the anvil.

29. *Lead and thallium* form a malleable globule.

30. *Bismuth and tin* unite readily, but the fused mass immediately throws out excrescences, and becomes covered with a dense crust of oxides. The reaction, however, is not so striking as with lead and tin.

31. *Thallium and tin* exhibit the same reaction as lead and tin, but the cauliflower-like excrescences are brownish-black. E. W. P.

Solution of difficultly soluble Substances. By A. H. ALLEN (*Analyst*, 1876, 139—141).—The method recommended is heating in a sealed tube with fuming hydrochloric acid: many substances are decomposed at 100°; many others at higher temperatures. Slag, basalt, and titanic iron sand, are among the substances mentioned as undergoing complete decomposition. Powdered red brick and tinstone were slightly dissolved. Chrome iron ore suffered little change. Hydrochloric acid is much preferable to sulphuric. M. M. P. M.

Comparative Analysis of Filter-papers. By A. GAWALOWSKI (*Zeitschr. Anal. Chem.*, xvi, 59—60).—Fresenius and Mohr having already pointed out (*ibid.*, xii, 148) the undue preference given to Swedish filter-paper over that prepared by several German firms, the author has analysed paper from nine different firms, and finds the Swedish, although superior as regards percentage of ash, inferior to that of one firm with respect to lightness; thus—

	Weight of filter.	Ash of ditto.	Per cent. of ash.
Sleicher and Stull, Düsen	0·281	·0013	0·46
Swedish (Blake and Cappus), Prague	0·306	·0008	0·26

All the papers contained iron, and cannot, therefore, lay claim to strict purity. C. L. F.

Determination of Sulphur in Coal. By W. MORGAN (*Analyst*, 1876, 151).—The ordinary processes were experimentally tested. Oxidation in the wet way does not give accurate results. The author prefers burning in oxygen and conducting the products into hydrochloric acid and bromine, with subsequent precipitation by means of barium chloride: any sulphur existing as sulphate remains in the ash.

M. M. P. M.

Volumetric Determination of Carbonic Acid. By G. W. Wigner (*Analyst*, i, 158).—Most laboratories are now furnished with the McLeod apparatus, or some similar efficient apparatus, for measuring the volume of gases under known conditions of temperature and pressure. The author has therefore devised a simple apparatus for the decomposition of carbonates and the measuring of the gas evolved. A test-tube of about 7 inches by 1 inch is taken and provided with a good india-rubber stopper bored with two holes. Through one of these holes a tubulated thistle-headed funnel of small size furnished with a stop-cock is passed, and through the other a bent piece of small-bore glass-tubing, also provided with a stop-cock. This bent tube is coupled to the McLeod or other gas-measurement apparatus by a short length (6 inches) of very stout, small-bore india-rubber tube ($\frac{1}{16}$ inch is large enough for the bore of this). In the bowl of the thistle-funnel a glass marble is put, and in the interior of the test-tube a smaller test-tube of about 2 in. × $\frac{3}{8}$, containing the sample to be analysed. The process is as follows:—The tubes of the McLeod apparatus are filled with mercury and the stop-cocks closed. The sample (say 25 grams of carbonate of lead) is weighed and transferred to the smallest tube, and about half an ounce of distilled water is poured into the large test-tube. The small tube is then carefully dropped in, taking care that its mouth is above the level of the water in the large tube; the stopper into which the funnel and bent tube have been inserted, is then carefully put in place, and the whole held in a slightly oblique position in a retort-stand clamp, on the ordinary rising table of the McLeod apparatus. The india-rubber tube is then coupled up to the facets of the measuring tube of the McLeod apparatus. The stop-cock on the bent tube is closed after having opened it and the cock on the funnel-tube, in order to liberate any excess of air in the india-rubber tube, and the mercury in the measuring tube is allowed to fall, so as to produce a vacuum. The stop-cock on the funnel remains open, and to the bottom of the test-tube a lamp is applied until the water boils briskly, when distilled water is poured into the funnel and kept from running into the test-tube by the pressure of steam; the boiling is continued until the steam escaping through the funnel and under the glass marble *all condenses*, showing that the tube is filled with pure steam. The lamp is now withdrawn and the stop-cock instantly closed. Meanwhile a portion of dilute nitric acid has been boiled on another burner, and is poured into the funnel. The stop-cocks on the bent tube and on the measuring tube are opened, and then the stop-cock on the funnel-tube is cautiously opened. The hot acid of course runs in, and the only precaution necessary is to avoid liberating the gas too quickly. When the test-tube is about two-thirds full, and all effervescence has ceased, the solution in the tube is again boiled, and then, still maintaining a partial vacuum by means of the mercury, the tube is filled completely through the funnel-tube with boiling distilled water, until every bubble of air is driven into the measuring-tube of the McLeod apparatus. The stop-cock on the bent tube is then shut, and the mercury in the pressure-tube and the measuring-tube brought to the same level. This brings the internal pressure of the air on the short india-rubber connecting tube to the atmospheric pressure, and as its volume does not exceed 1 c.c. the correction for its temperature may be safely omitted. The gas is then measured in the ordinary way and its volume calculated to weight and percentage.

It is easy to make four determinations of carbonic acid per hour by this apparatus, and the accuracy of the results is very great.

D. B.

Schoenbein's Test for Nitrates. By F. STORER (*Amer. Jour. of Sci.* [3], xii, 165—176).—In a paper by Carius (*Liebig's Annalen*, 1874, clxxiv, 14), he remarks incidentally that he has not found Schoenbein's iodo-starch test for nitrates with zinc as the reducing agent, a specially delicate one. F. H. Storer has recently examined this point, and thinks the difficulty found by Carius to lie in the manipulation of the test, since he performs the reaction by adding dilute sulphuric acid and iodo-starch paste directly to the nitrate solution, and then stirring with a zinc rod, instead of first reducing the neutral nitrate solution by zinc or cadmium, thereafter acidulating with dilute sulphuric acid, and finally adding the iodo-starch paste. The defect in the test, as hitherto used, Storer thinks to be due to the formation of hydric peroxide, even in water free from nitrates or nitrites, when treated with zinc or cadmium. He finds that when the degree of colour of the iodo-starch obtained is less intense than the tint obtained from 0·0001 gram N_2O_5 (= 0·0000187 gram KNO_3) in 50 c.c. water, it is difficult to decide whether this may not be wholly due to H_2O_2; it is possible, at all events, to get as much H_2O_2 by boiling cadmium, zinc, or amalgamated zinc with water alone, as will give a reaction with acidulated iodo-starch equal to that obtained from 0·00005 N_2O_5. This the author has confirmed experimentally. With pure water the results were constant, but in the case of water taken from wells, and of rain water from brick or lead cisterns, no reaction was at first obtained on simply boiling the water with cadmium, but when it was left over the cadmium for 24 hours, H_2O_2 was finally obtained in the rain-water. The author also shows in this paper that methods for detecting nitrates depending on the volatility of the nitrous acid may be vitiated by the transference of H_2O_2 with the vapour of water. With regard to the delicacy of the iodo-starch test for nitrates, supposing there to be interference from H_2O_2, the author advises the method of procedure in which the nitrate is reduced by itself as a preliminary step, before the acidulation of the liquid or addition of the iodo-starch. He has also employed metallic cadmium in slightly acidulated water for the reduction of nitrates to nitrites with very good results; 0·0005 gram N_2O_5 gave a strong coloration almost immediately; 0·0002 gram N_2O_5 similarly in about five minutes; 0·0001 gram N_2O_5 gave a reaction in about fifteen minutes. Pure water acidulated with H_2SO_4 gave a reaction after standing over night. To determine whether metallic cadmium in acidulated water actually destroys H_2O_2 at 100°, pure water was boiled with cadmium and left to stand for some hours in contact with the metal; this solution was then divided into two portions, one tested directly with iodo-starch, plus acid, whilst the other was acidulated and again boiled upon cadmium. In the first case a strong reaction was given, whilst in the second no coloration became evident till after standing two hours, and then it was but slight. Hydrogen was found to have little or no effect in destroying the H_2O_2. J. M. T.

Determination of Potassium as Potassium Platinochloride, in presence of the Chlorides of the Metals of the Alkaline Earths. By R. FRESENIUS (partly after experiments by A. SOUCHAY) (*Zeitschrift. Anal. Chem.*, xxvi, 63—65).—This method, at the commencement, does not differ from that usually employed. The concentrated solution is treated in a small porcelain dish, with excess of pure platinum chloride in excess, evaporated on a water-bath (below 100°) to a syrupy consistence, carefully mixed with alcohol of 80 per cent., and left a short time with frequent stirring. By this means the platinum-potassium chloride, insoluble in alcohol, is separated from the sodium salt, which goes into solution.

At this stage the method begins to differ from the usual one. The alcoholic solution is poured through a small filter, and the residue in the dish treated with alcohol, till the potassium salt appears pure. This is then collected on the filter and washed thoroughly with alcohol of the same strength. The filter is then dried, to ensure the complete expulsion of the alcohol. If the quantity of the salt thus collected be large, it may be separated as much as possible from the filter-paper, from which the remaining salt is removed by boiling water; the solution is then evaporated to dryness in a small platinum dish. The main bulk is then added, the whole dried at 130°, and weighed. If the quantity is small, the precipitate may be wholly washed off the filter into the platinum dish, evaporated, and weighed as above.

To ascertain whether the weighed potassium-platinum salt is pure, treat it with repeated quantities of hot water, leave it to settle, and decant the solution into a dish. A little platinum chloride is then added, to convert any sodium chloride into the platinum-sodium salt, the solution evaporated as above almost to dryness, and mixed with alcohol of 80 per cent. The deposited potassium salt is filtered off and washed with alcohol, dried on the filter, and washed with boiling water in a platinum dish, into which the undissolved bulk of the original precipitate is brought. The whole is evaporated to dryness, dried at 130°, and weighed. Should any alteration in weight have taken place, the previous precipitate was impure, and the present weight may be regarded as the right one. Pure platinum-potassium chloride must dissolve entirely in boiling water.

As regards the accuracy of the above method in presence of other alkaline salts, the following results are instructive. In a solution of potassium chloride, the potassium was determined as above, at first in the normal solution, then with addition of chlorides of barium, strontium, calcium, and magnesium respectively. The results show that the method maintains its accuracy in presence of the chlorides of any of the alkali-metals; but that when magnesium, barium, and strontium respectively are present, the results were very slightly in excess. To obtain perfectly accurate results, therefore, the process recommended above should always be resorted to. C. L. F.

On Schaffner's Method of Estimating Zinc. By F. A. THURN (*Chem. Centralbl.*, 1876, 588—590).—This method consists in dissolving the substance containing zinc in ammonia, and titrating with sodium sulphide, the end of the reaction being known by the blackening of a little ferric hydrate suspended in the liquid. The best way of making the ferric hydrate for this purpose is to dissolve 3 grams of iron in nitro-hydrochloric acid, and dilute to 100 cub. cents. A few drops of this solution are dropped into 1 or 2 cubic centimeters of strong ammonia in a small crucible, and the mixture is added to the solution of zinc. The conditions of success of the process are a nearly constant volume of liquid, about 400 cub. cents.; careful determination of the amount of sulphide necessary to turn the ferric hydrate black. Oxides of the alkaline earths are without influence on the reaction. If heavy metals are present, the zinc is most conveniently separated by the ordinary processes, and precipitated from its solution in acetic acid. Usually, however, only copper, lead, manganese, and iron have to be removed.

If organic matter be present, it is removed by ignition. Lead and manganese are not precipitated as sulphides till all the zinc has come down, and the iron begins to give a black coloration. But the precipitation of the manganese as hydrate exercises a disturbing influence on the accuracy of the indicator; it is therefore better to remove manganese with bromine, or potassium permanganate, till a coloration just becomes apparent. The manganese is thus all precipitated as manganic hydrate thus:—

$$Mn_2O_7 + 8MnO = 5Mn_2O_3.$$

Lead is determined as sulphate, and copper by the colorimetric process. If much iron be present, some zinc is carried down during the precipitation of the iron as hydrate. The precipitate must therefore be redissolved, and the ferric hydrate again precipitated with ammonia.

Zinc may be obtained sufficiently pure for adjusting the strength of the standard solution, by melting commercial zinc and allowing it to oxidise on the surface; the oxide is scraped off with a piece of wood. Half the melted metal is then poured into another crucible, and the operation repeated. The zinc thus obtained is almost chemically pure, and dissolves in acid without leaving a residue. W. R.

Assay of Zinc Ores. By A. MASCAZZINI and J. G. PARODI (*Gazzetta chimica italiana*, vi, 537).—The authors have succeeded in causing electro-deposited zinc to adhere to platinum, under conditions similar to those for the electrolytic assay of copper, cobalt, and nickel. This renders the method applicable to the assay of zinc ores, and the experiments made with various ores leave no doubt as to the superiority of the process. C. E. G.

On the Estimation of Arsenic as Pyroarsenate of Magnesia.

By B. BRAUNER (*Zeitschrift anal. Chem.*, xvi, 57—58).—The method of determining arsenic as magnesium arsenate, has long been recommended. The moot question is, however, whether it be preferable to weigh the precipitate on the filter, or to convert it into the pyroarsenate.

Both methods are open to objection; the first on account of the multiplicity of weighings, and possible loss of water by slight excess of temperature; the second, because of the unavoidable loss of arsenic on igniting the filter paper.

Wood (*ibid.*, xiv, 356) meets these objections, as well as that of the perceptible solubility of the magnesium arsenate, by adding alcohol, reprecipitating, and weighing the filter-paper, with as much of the precipitate as cannot be transferred to a double porcelain crucible. In this, after the addition of a few drops of nitric acid, it is converted, by first gently then strongly igniting, into the pyro salt.

The author recommends the following method, which he has employed for some time with very good results. The precipitation is effected with magnesia mixture, and the addition of half its bulk of alcohol. The solution is allowed to stand over night, and decanted; the precipitate is dissolved in HCl, reprecipitated as before, thrown into a small filter, and washed with a mixture of 1 vol. ammonia, 2 vols. of alcohol, 3 of water. When dried, it is introduced as completely as possible into a small porcelain crucible included in a larger platinum one, moistened with nitric acid, covered and heated, at first gently, afterwards to a bright redness. The residue on the filter is washed into a rather large porcelain crucible, with a little nitric acid and water, the liquid evaporated, and the residue heated as before, and weighed as pyroarsenate. The results are accurate. C. L. F.

Estimation of Antimony in Alloys.

By E. H. BARTLEY (*Chem. Centr.*, 1876, 39).—The alloy is decomposed by nitric acid; excess of acid is neutralised by ammonia; and the whole is digested with yellow ammonium sulphide, until the antimony is entirely dissolved. The solution, after filtration, is digested with hydrochloric acid until sulphuretted hydrogen ceases to be evolved, and the supernatant liquid becomes clear; the precipitate is collected, washed free from hydrochloric acid, and removed from the filter to a beaker. The filter is washed with bromine, which is again removed by means of water. The contents of the beaker are heated with a little nitric acid free from hydrochloric acid; if any sulphur remain unoxidised, a little more bromine is added. The contents of the beaker are evaporated to a small bulk, transferred to a porcelain crucible, evaporated to dryness, ignited, and weighed as Sb_2O_4. M. M. P. M.

Solution of Molybdenum in Nitric Acid.

By H. NELSMANN (*Zeitschr. Anal. Chem.*, xvi, 52, 53).—The author imputes the formation of an insoluble precipitate in solutions of ammonia molybdate, pointed out by Jungck (*ibid.*, 15, 290) to silicious or other impurities in the nitric acid. That it is not due to the action of light is shown by the fact that a 6 litre white glass bottle-full of the solution was exposed to the sun for five weeks, not the slightest alteration being produced in the liquid. The following is a good method of restoring the molybdate solution.

The solution is precipitated with sodic phosphate, the precipitate dissolved in ammonia, the solution precipitated with magnesia mixture, filtered, and the filtrate evaporated, when the yellow ammonia molybdate forms in yellow crusts. This, dissolved in 3 parts of ammonia, and poured into 15 parts of nitric acid, forms the solution ready for use.

Note by Fresenius.—The formation of a yellow precipitate in the most carefully prepared molybdate solutions cannot be denied, and requires investigation. C. L. F.

The Manganese in Ashes detected as Manganese Phosphate. By G. CAMPANI (*Gazzetta chimica italiana*, vi, 464—466).—The manganese usually occurs in the ash in the state of oxide, or a salt such as a silicate. In order to detect it, if the ash contains sufficient phosphates, it is merely necessary to treat it with warm nitrohydrochloric acid, filter, and evaporate to dryness on the sand-bath, when the residue, if any manganese be present, will acquire a more or less pronounced amethyst colour. Those ashes which do not contain phosphates, after being exhausted with hot water, are boiled with a mixture of phosphoric and nitric acids in the proportion of 85 parts by measure of the latter to 15 of syrupy phosphoric acid. The clear liquid is then evaporated as before. By this means the manganese in the ashes of wood, corn, tobacco, &c., can be easily detected. The process is also applicable to manganiferous minerals. C. E. G.

Determination of Iron Oxide and Alumina in presence of Phosphoric Acid. By H. PELLET (*Bull. Soc. Chim.* [2], xxvii, 106).—From the results given in a preceding paper, a method has been devised for the determination of iron and alumina in presence of phosphoric acid. To the liquid containing phosphoric acid, alumina, and oxide of iron, an excess of calcium chloride is added, and then ammonia; this precipitates tricalcic phosphate, alumina, and ferric oxide. The precipitate is ignited and weighed. It is then dissolved in hydrochloric acid, and in one portion of the solution the phosphoric acid is determined by means of uranium, and in another portion the iron by stannous chloride. The phosphoric acid is calculated into tricalcic phosphate, and the iron into Fe_2O_3, and the difference between their combined weight and that of the original precipitate gives the alumina.

If sulphuric acid is present, it must be separated by baryta before the addition of ammonia. The presence of baryta in the filtrate does not affect the results, provided sufficient calcium-chloride is added to precipitate all the phosphoric acid, as $P_2O_5(CaO)_3$. H. H. B. S.

Estimation of Iron by Stannous Chloride. By H. NELSMANN

(*Zeitschr. Anal. Chem.*, xvi, 50—52).—Two objections have been made to the method of estimating iron by means of standard solutions of stannous chloride, recommended by Fresenius and others. First, that the solution of tin chloride rapidly decomposes, and has constantly to be re-standardised; secondly, that the results are not constant, the same weight of ore requiring varying amounts of standard solution.

The first objection is met by employing for the conservation of the standard solution a bottle to which the air can have access only through a wash-bottle of potassium pyrogallate. When the solution is kept in this manner, the variation in four weeks is under 0·1 c.c. The second objection is invalid, as, when the solution is strongly acid and hot, the limits of error can be confined to 0·05 c.c. The extreme sharpness, and above all the rapidity of the operation, render it preferable to any other, especially in mining districts. From the time of weighing the solution, boiling and titration do not occupy more than five minutes. C. L. P.

Iron Analysis. (*Dingl. polyt. J.*, ccxxiii, 325).—Lill and Sturm have examined a sample of puddled steel (I) and natural steel (II), with the following results:—

	C.	Si.	P.	S.	Mn.	Co.Ni.	Cu.	Slag (Fe_2O_3?).
I...	·758	·048	·019	·002	·180	·003	·005	1·217
II...	·899	·029	·019	·005	·043	traces	·004	·633

The determination of slag and ferric oxide was made according to Eggertz' method with bromine, treating the residue with a solution of sodium carbonate.

The residue in the above analyses consisted of SiO_2, viz., 0·180 for (I), and 0·050 for (II), while the remainder, viz., 1·037 for (I), and 0·583 for (II), consisted of ferric oxide, and very small quantities of manganese. D. B.

Analysis of Plating and Gilding Solutions. By A. H. Allen (*Analyst*, i, 178).—A definite measure of the sample liquid is largely diluted with water, and the whole heated to boiling. Sulphuretted hydrogen is then passed through the liquid. The silver falls as a black sulphide which filters and washes well, and is commonly said to be free from copper. This, however, is not always the case, while any zinc that may have been present is sure to be thrown down. On this account it is recommended to rinse the washed sulphide of silver off the filter into a flask or beaker, and treat it with excess of bromine water, which converts it rapidly and completely into silver bromide. Boiling water is now added and the silver bromide washed, dried, fused, and weighed. For determining the gold, the following method is described:—A measured quantity of the gilding solution is introduced into a porcelain crucible and cautiously concentrated. When it is in a syrupy condition, a few grams of pure red lead or litharge are added, and the evaporation is continued to complete dryness. The crucible is covered and raised for a short time to a moderate red heat. The oxide of lead is reduced by the cyanide present (in gilding solution) with production of metallic lead and cyanate, and the reduced metal unites with the gold. The resultant button of metal is separated from the slag, and the gold obtained either by cupellation or treatment with pure nitric acid. Electro-silvering solutions can be analysed in a precisely similar manner, but, of course, in this case, treatment of the rich lead with nitric acid is inadmissible, and cupellation must be resorted to. D. B.

Adulteration of Sodium-palladium Chloride with Sodium Chloride. By A. Gawalowski (*Zeitschr. Anal. Chem.*, xvi, 58—59).—In a sample of palladium-sodium chloride, in which by qualitative examination no impurities could be detected, quantitative analysis showed adulteration with sodium chloride to the amount of 22 per cent. Fresenius' method of preparation might introduce an excess of sodium chloride, not exceeding 6 per cent. at the utmost, so that, in this case, wilful adulteration must have been resorted to.

So skilful was the admixture, that even a lens failed to detect it. But on treatment with water, the palladium-salt readily dissolved, leaving the impurity behind in little cubes. C. L. F.

A Method of Estimating the Halogens in Organic Compounds. By W. Klobukowski (*Deut. Chem. Ges. Ber.*, x, 290—292).—This is a modification of E. Kopp's method of estimating chlorine, bromine, and iodine in organic compounds. The method is based upon the fact that when such compounds are heated with ferric oxide, they yield ferric chloride, bromide, or iodide, which, after reduction to ferrous salt, may be decomposed by means of sodium carbonate, whereby the halogen is obtained in the form of sodium salt.

The author proceeds as follows:—A weighed quantity of the substance to be analysed is intimately mixed in a porcelain mortar with pure ferric oxide (obtained by heating pure ferrous sulphate to redness in the air), and introduced through a small glass funnel into a hard glass tube 60 cm. long, 5—6 mm. in diameter inside, somewhat less than 1 mm. thick, and closed at one end. The mortar is carefully rinsed out with fresh portions of the oxide, and the rinsings are introduced into the tube, so that 20—25 cm. of its length is thus filled. A spiral of fine pianoforte wire, 20—25 cm. long, is next introduced, and the remaining space is filled with dehydrated sodium carbonate. The tube is then placed in a combustion furnace, with that portion which contains sodium carbonate for the most part projecting. The metallic iron is first heated to redness, and then the heating is gradually extended to the mixture in the after part of the tube. The decomposition is complete in 5—10 minutes. While the tube is still hot (but no longer red-hot), it is removed from the furnace, wiped rapidly with a dry cloth, closed with the finger, and plunged into a tall beaker one-fifth full of water, whereupon the hot part of the tube breaks into small fragments: the cold part, containing sodium carbonate, is washed out with distilled water. The contents of the beaker are heated in the water-bath for 30—40 minutes; the liquid is filtered, and the residue washed with hot water. Finally, the sodium chloride, bromide, or iodide thus obtained is precipitated with silver nitrate in the ordinary manner. The results given show that the process is accurate. The method may also be used with advantage to detect the halogens in organic compounds. J. R.

Estimation of Sugar. By R. SACCHSE (*Chem. Centr.*, 1876, 520).—18 grams of pure and dry mercuric iodide and 25 grams of potassium iodide are dissolved in water; a solution of 80 grams of caustic potash is added, and the whole is made up to 1 litre. 40 c.c. of this solution (= 0·72 gram HgI_2) are boiled in a basin, and a solution of pure grape-sugar is run in until the whole of the mercury is precipitated. The final point is determined by spotting a drop of the supernatant liquid on a white slab and there bringing it into contact with a drop of a strongly alkaline solution of stannous chloride. The production of a brown colour shows the presence of unprecipitated mercury.

The author finds that the prepared mercury solution acts in different ways towards inverted and towards grape-sugar. Fehling's copper solution has the same action on both. By standardising the prepared mercury solution against pure grape-sugar, and also against inverted sugar, it is possible to determine the quantities of these sugars simultaneously present in a liquid. It is only necessary to determine the number of cubic centimeters of the liquid required to precipitate completely the mercury from 40 c.c. of the standard solution, and then to determine, by means of Fehling's solution, the quantity of sugar of the formula $C_6H_{12}O_6$, which is present in the liquid under examination.

The necessary calculation is made on the principles of indirect analysis. So also it is possible to determine whether a substance which is without direct reducing action is cane-sugar or dextrin. It is only necessary to invert by boiling with acid, and to make two determinations, one with the standard mercury solution, the other with Fehling's solution: the presence of inverted sugar points to cane-sugar, of grape to dextrin, in the original liquid.

M. M. P. M.

Action of Sodic and Calcic Hypochlorites upon Urea. By YVON (*J. Pharm. Chim.* [4], xxiv, 209—214).—The *Journal de Pharmacie et de Chimie* for July, 1876, contains an account of a method for the determination of urea, published by Jaillard in the *Mémoires de Pharmacie Militaire*, the peculiarity of which consists in the substitution of hypochlorite of calcium for that of sodium. The author has studied the action of both these salts upon urea in order to compare them with that of sodium hypobromite. He has found that—

1st. Sodium hypobromite disengages all the nitrogen from urea in the cold.

2nd. Sodium hypochlorite disengages about 67 per cent. in the cold, and 92 per cent. on heating.

3rd. Calcium hypochlorite disengages about 94·5 per cent. in the cold, but the quantity is not always precisely the same. On heating, more gas is given off than the quantity of urea experimented upon could yield of nitrogen.

The author concludes that in the analysis of urea by decomposition into its elements, calcium hypochlorite does not give exact results, but that for an approximate analysis it is preferable to sodium hypochlorite, since the action takes place in the cold and with greater rapidity.

H. H. B. S.

Simple Method for Estimating the Value of Commercial Samples of Salicylic Acid, and of Detecting it in Milk and similar Organic Solutions. By Dr. Muter (*Analyst*, i, 193).—A standard solution of pure salicylic acid (1 gram of acid dissolved in a litre of water, so that 1 c.c. represents 1 mgm. of acid), is prepared; the *indicator* solution consists of a solution of pure neutral ferric chloride of such a strength that 1 c.c. added drop by drop to 50 c.c. of standard acid, just ceases to give any increase in intensity of colour. 1 gram of the commercial sample is then dissolved in 1 litre of water, and 50 c.c. is put into a Nessler tube; to this, 1 c.c. of ferric solution is added, and the colour observed after standing for five minutes: some of the standard acid is also poured into another tube and made up to 50 c.c. with water, and the 1 c.c. of ferric chloride added: when the colours are alike, the amount of pure acid present in the sample is equal to the amount of pure acid added. All mineral acids should be absent; even acetic acid affects the reaction. To detect the presence of salicylic acid added to beer or milk, four ounces of these liquids are dialysed for twelve hours in a pint of distilled water; if after that time salicylic acid is still found to be present, the dialysis must be continued for 48 hours. The amount present is determined in the manner above-stated.

E. W. P.

Testing Gaultheria Oil. (*Chem. Centr.*, 1876, p. 30).—Sassafras oil is detected by adding 3—4 drops of nitric acid (sp. gr. 1·3 to 1·4), to 4—5 drops of the oil. Pure gaultheria oil is unchanged at first, but after some hours, solidifies to a mass of colourless crystals (nitromethyl salicylic acid): sassafras oil becomes blood-red in colour, and soon changes to a brownish amorphous mass. Chloroform is detected by the smell when the liquid is warmed.

M. M. P. M.

Detection of various Colouring Matters in Wine. By A. Dupré (*Analyst*, i, 193).—Fraudulent colouring matters added to red wines may be detected by dialysis, which is best accomplished by placing in the wine a cube of jelly about $\frac{3}{4}$ in. square: these cubes are made by dissolving 5 grams of gelatin in 100 c.c. of warm water, and pouring the solution into flat paper moulds; from the plate thus obtained, the cubes are cut. After 24 to 48 hours, the cube, on examination by transmitted light, will be found to be coloured, more or less deeply, by any colouring matter present, excepting the natural colouring matter, which penetrates only to a depth of $\frac{1}{8}$ in. at the most. The nature of the colouring matter may be determined either by the colour of the jelly, or spectroscopically, or by the action of dilute ammonia. The colouring matters which penetrate jelly but slowly are those of pure wine and of rhatany-root; whereas rosaniline, cochineal, logwood, brazilwood, indigo, litmus, red cabbage, beet-root, *Malva sylvestris*, and *Althea officinalis* penetrate rapidly into jelly. E. W. P.

Composition of Commercial White Lead. By G. W. WIGNER and R. H. HARLAND (*Analyst* i, 208—211).—Lead carbonate and hydrate, which form *white lead*, must, to produce a good paint, be present together in definite proportions, so that the hydrate forms a paint instead of an emulsion. Having experimented on paints made of lead hydrate and carbonate alone, and of these two mixed in various proportions, none of which were successful, the authors came to the conclusion that 25 per cent. of lead hydrate is necessary to produce a white paint of good body. E. W. P.

New Method of Estimation of Pure Anthracene in Crude Anthracene. By MEISTER, LUCIUS, and BRUNING (*Zeitschr. Anal. Chem.*, xvi, 61—62).—1 gram of the crude anthracene is heated to boiling, without loss, with 45 c.c. glacial acetic acid, in a flask of about 500 c.c. capacity. While the liquid is kept constantly boiling, a solution of 15 grams of chromic acid in 10 c.c. of glacial acetic acid, and 10 c.c. water is added. The addition should extend over two hours, and the boiling be kept up for two hours more. The flask and contents are allowed to stand twelve hours, and the solution mixed with 100 c.c. water is again left for three hours.

The separated anthraquinone is collected on a filter and washed with water, at first cold, then slightly alkaline and boiling, then pure and boiling. The contents of the filter are washed into a little porcelain dish and dried at 100°. When dry it is treated with ten times the quantity of fuming sulphuric acid (68° Baumé), and heated for ten minutes at 100°.

The solution of anthraquinone thus prepared is poured into a wide dish, and placed, for the absorption of water, for twelve hours in a damp place. 200 c.c. of cold water are then added, the separated anthraquinone collected, and washed as above. From the filter it is washed into a small dish, dried at 100°, and weighed. The dish is heated till the anthraquinone is completely volatilised, and then weighed, together with the residual impurities. The difference between the two weights gives the anthraquinone which is calculated into anthracene in the usual way. C. L. F.

Testing Fatty Oils. By G. MERZ (*Chem. Centr.*, 1876, p. 8).—If an adulterated oil be mixed with genuine oil of the same species as itself, streaks appear in the liquid: if the oil under examination be genuine, these streaks do not make their appearance. Equal quantities of the oil to be tested and of a pure sample of the same oil are placed in test-tubes, which are immersed in water for a few minutes, the two oils are then mixed: and if streaks appear, the sample is adulterated. M. M. P. M.

Testing Olive Oil. By G. MERZ (*Chem. Centr.*, 1876, p. 7).—A drop of the oil is placed in a very small hollow made by the sand-blowing machine in the centre of a glass plate: the plate is maintained at a temperature of about 100° for 12 hours or so. Olive oil remains almost unaltered: linseed, or other drying oil, assumes the appearance of a hard gummy mass. M. M. P. M.

On Methods of Estimating Methyl Alcohol in the Manufacture of Colouring Matters. By G. KRAEMER and M. GRODZKI (*Deut. Chem. Ges. Ber.*, ix, 1928—1932).—According to Krell (this Journal, xii, 291) 5 c.c. of wood-spirit containing 100 per cent. of methyl alcohol, when treated with phosphorus di-iodide, yield 7·2 c.c. of methyl-iodide. This differs from the theoretical quantity 7·8 c.c., and the authors endeavour to account for the deficiency. They prepared pure methyl alcohol from the formate, which is prepared by digesting methyl alcohol with formic acid of specific gravity 1·22. From this alcohol they obtained 7·45. of methyl iodide, the difference ·35 c.c. from the normal amount 7·8 c.c. being referred to formation of methylphosphine, and the vapour of methyl iodide which remains behind in the apparatus.

The difference between this result and that of Krell's and of the former observations of the authors depends on the fact that methyl alcohol prepared from the oxalate or benzoate and dried over caustic baryta is not anhydrous, and that there must also have been some admixture of foreign bodies with the alcohol used in previous investigations. Distillation over sodium is much preferable to the use of baryta. The foreign bodies must have been formed by the long continued action of alkalis on the ether or the free methyl-alcohol.

With regard to the presence of bodies in wood-spirit which form methyl iodide, but have no methylising action on aniline, the authors point to the fact that they have shown that methyl-acetal is a constant constituent of wood-spirit; and since its boiling point is nearly identical with that of methyl-alcohol, they have examined it in its behaviour to the iodine test. Methyl-acetal was prepared by heating methyl-alcohol, aldehyde, and acetic acid in sealed tubes, shaking up the mass when cool with caustic soda, treating it with fused caustic potash, and finally distilling it over a fresh quantity of this reagent. From 5 c.c. of this methyl-acetal 5·3 c.c. of methyl iodide were obtained, which shows that only the two methyl groups were split off as methyl iodide, and that the aldehyde was not converted into alcohol. In using the technical method of testing methyl-alcohol, this must be borne in mind. For instance, a mixture of 10 per cent. of methyl-acetal and 90 per cent. of methyl-alcohol would give with the number above, $\frac{5·3 \times 10 + 7·45 \times 90}{100} = 7·23$ c.c. of methyl-iodide, which would show 97·1 per cent. of methyl-alcohol.

A new method for testing methyl-alcohol proposed by the authors depends on the estimation of the gas-volume-weight of the alcohol. Since the components of the methyl-alcohol used for technical purposes, such as acetone, dimethyl-acetal, methyl-ethyl ketone, &c., have a much higher vapour-density, it seems possible to estimate the purity of the alcohol by the vapour-density. The vapour-density of dimethyl-acetal being 45, a methyl-alcohol containing 10 per cent. of this body should give $\frac{16 \times 9 + 45 \times 1}{10} = 18\cdot9$ instead of 16. A mixture of 1 volume of methyl-acetal and 9 of methyl-alcohol gave 17·7 instead of 18·9; and a mixture of equal volumes of the two gave 23·9 instead of 31·2.

Further researches will be undertaken to show why acetal alone yields the correct vapour-density, but not when mixed with methyl-alcohol.
G. T. A.

Ammonium Sulphomolybdate as a Test for Alkaloïds. By T. B. NAGELVOORT (*Arch. Pharm.* [3], ix, 249—254).—The reagent is prepared shortly before use, by adding 0·5 gram of ammonium sulphomolybdate to 8 grams of chemically pure sulphuric acid, and warming the milky solution till it becomes clear. It gives the following colour reactions, with different alkaloïds:—

Quinine.—A clear green colour, changing to a colourless solution in half-an-hour.

Strychnine, Atrophine, and *Santonine.*—Remains colourless.

Veratrine.—Becomes dirty-brown, changing through grey to blue, and finally turning a permanent yellowish-green.

Narcotine. Turns bright yellowish-green, quickly becoming colourless.

Morphine.—Becomes purple-red, and soon changes through violet to a magnificent dark blue. After standing, it becomes first green and then colourless. Less than one-hundredth of a milligram can be detected by its use.

Brucine.—Takes a brick-red colour, turning yellow, and then slowly decolorising.
E. N.

On the Separation of the Alkaloïds. By E. RENNARD (*Chem. Centr.*, 1876, 456).—For legal purposes, a rapid and simple method for the separation of the alkaloïds is required. The portions of the corpse to be examined are treated with 90—94 per cent. alcohol, acidified with sulphuric acid; or, if there be much fat present, with water, and the whole heated on a water-bath. After decantation of the alcohol, the residue is treated with fresh alcohol, which is afterwards added to the first portion. After completely cooling, which allows of easier filtering, the liquid is filtered, and then distilled, the residue being finally heated on the water-bath with water, so as to free it completely from alcohol; and on further addition of water it is again filtered, thus separating the fats, which should be well washed with acidulated water. If saccharine or mucilaginous substances are under examination, neither water nor alcohol can be used, owing to the formation of syrup—nor ether or benzene, because of the formation of an emulsion. It is recommended that a fourth or third of its volume of ether be added to the acidulated alcohol, which suffices to precipitate the sugar, and not the alkaloïds. By the above method the alkaloïds may be separated easily, and perfectly pure, provided that the liquids before filtering are allowed to settle and become quite cool. The solutions made alkaline by ammonia may be treated with alcohol, free ether, or benzene. The final extraction is made with acetic ether in preference to amyl alcohol, which dissolves a larger amount of colouring matter. For the identification of the alkaloïds in the various extracts, the reader is referred to Dragendorff's papers on this subject. E. W. P.

Determination of Morphine in Opium. By E. F. TESCHEMACHER (*Chem. News*, xxxv, 47).—In employing the following method the use of alcohol to extract the morphine is avoided, and meconic acid is separated at an early stage, which prevents the formation of a basic meconate on precipitation of the morphine. Two special reagents are required for this process: the one prepared by mixing 1 part of solution of ammonia, sp. gr. 0·880, with 20 parts of methylated alcohol and digesting in this mixture a large excess c morphine, this when filtered is termed "*morphiated spirit;*" the other, "*morphiated water,*" is water saturated with excess of morphine, and contains 0·04 per cent. of this alkaloïd.

1,000 grains of opium are macerated for twelve to twenty hours in about 4,000 grains of cold distilled water together with 300 grains of lead acetate, stirring the mixture from time to time. This separates the meconic acid as lead meconate, whilst the morphine is dissolved in the acetic set free.

After this maceration the opium may be readily ground in a mortar to a paste, and so much more cold distilled water added, rinsing the pestle and mortar with successive portions of it, as to fill with the mixture a measure = 20,250 grains of distilled water: experience has shown that the space occupied by the insoluble matters measures from 200 to 300 grains, so that the limit of possible error, by averaging and allowing 250 grains for the insoluble portion, amounts to 0·05 per cent. in opium containing 10 per cent. of morphine. The mixture is to be filtered and 15,000 measured grains, = 750 grains of opium, of the clear solution are to be evaporated to an extract on a water-bath, and this residue to be drenched with 3,090 grains of boiling alcohol or methylated spirit, and the whole digested, with frequent stirring for about ten minutes. This separates the gum, &c., of the opium, which is insoluble in alcohol, and so far frees the solution of morphine from impurity. At this stage of the process it is well to get rid of the excess of lead-salts, and for this end sulphuric acid is preferable to sulphuretted hydrogen. So much diluted sulphuric acid as may be equal to 30 grains of oil of vitriol will almost always be sufficient for this purpose, any excess of acid being converted into sulphate of ammonia by the subsequent addition of so much solution of ammonia as shall be equivalent to the 30 grains of oil of vitriol, thus forming a salt but slightly soluble in the alcoholic solution. This mixture may now be transferred to a beaker and allowed to settle for twelve hours, after which it is to be filtered and the filter and insoluble residue thoroughly washed with alcohol or methylated spirit. This alcoholic filtrate is then distilled, or evaporated on a water-bath, to about 1,000 grains; and mixed, while still hot, with 400 grains of solution of ammonia, sp. gr. 0·880, stirring rapidly and continuously for at least twenty minutes, whilst the beaker or evaporating dish should be cooled as rapidly as possible, by immersion in an external vessel filled with cold water. The rapid and continuous stirring is most important, as the precipitation of the whole of the morphine *in fine powder* is thereby effected, instead of the granular or mammillated condition so frequently met with, and it thus permits of the easy and thorough separation of all the narcotine which may be mixed with the morphine. When the cooling of the mixture and precipitation of the morphine is thus attained, transfer it quickly and completely to a filter of sufficient capacity to hold the whole, and when the liquid portion has passed through, wash the remainder of the precipitated morphine adhering to the dish or beaker on to the filter, using for this purpose the morphiated spirit already described, and continuing the washing of the precipitate until it is completely freed from the mother-liquor. To do this effectually requires some little care: thus the morphine on the filter must be kept in a spongy condition and never allowed to cohere, which is easily effected by pouring the morphiated spirit round the edges of the filter so as not to disturb the precipitate, which must not be permitted to drain or solidify until this washing is completed.

The precipitate is now to be washed from off the filter-paper with the morphiated water previously described, and digested therein for a few minutes, which removes some more colouring matter together with any salts soluble in water but insoluble in alcohol, which may have adhered to the precipitated morphia; then once more collect the precipitate on a filter, washing it with morphiated spirit, after this once with ether, and finally thrice or more with benzene; this completely frees it from narcotine, which is very soluble in benzene, morphine on the contrary being insoluble in this liquid. It now remains to drain and dry at a low temperature, say 100° F., the resulting pure and white morphine, the weight of which will indicate the amount of this alkaloïd present in 750 grains of the opium under examination.

E. W. P.

Testing of Vinegar, Coffee, Pepper, and Beer. By A. HILGER (*N. Rep. Pharm.*, xxv, 514—520).—Strohl's test for mineral acids in vinegar, based upon the solubility of calcium oxalate in mineral acids and the insolubility of the same salt in acetic acid, is not, according to the author, of any great delicacy. The fact that methylaniline is not changed by acetic acid, but is coloured greenish-blue by mineral acids, may be employed as a most delicate qualitative test. Quantitatively applied, as proposed by Witz, the process fails in delicacy. On evaporating the vinegar under examination, together with a few drops of a dilute methylaniline solution, the colour changes to greenish-blue, if $\frac{1}{10}$ to $\frac{1}{20}$ per cent. of sulphuric or hydrochloric acid is present.

The ash of pepper varies from 5·5 to 6·0 per cent.

The presence of Prussian blue in certain kinds of coffee berries is confirmed.

The analyses of beers given are only of local interest.

M. M. P. M.

Detection of Picric Acid in Beer. By D. VITALI (*Gazzetta chimica italiana*, vi, 466—467). The author considers amylic alcohol to be the best means of abstracting picric acid from beer adulterated with it; 10 cub. cent. of beer are agitated with half its volume of amylic alcohol, the latter being removed by means of a pipette, filtered, and evaporated; a yellow residue indicates picric acid. This is dissolved in a small quantity of water, and divided into four portions, which are severally treated with ammoniacal copper sulphate, potassium cyanide, ammonium hydrosulphide, and potassium nitrate; if picric acid is present, these give the crystalline ammonium copper picrate, the purple red isopurpuric acid, picramic acid, and the yellow crystalline potassium picrate. C. E. G.

Determination of Nitrogen in Milk and its Educts. By G. Musso (*Gazzetta chimica italiana*, vi, 391—402). The unsatisfactory results obtained in the determination of nitrogen in albuminous compounds by Will and Varrentrapp's method, which the author discusses at length, induced him to undertake a comparison of the amount of nitrogen obtained by Will and Varrentrapp's method, and by that of Dumas. The substances operated on were milk, whey, cheese, and aqueous and alcoholic extracts of the latter; in every case a considerable deficiency in the nitrogen was observed when the analysis was made by Will and Varrentrapp's method, as compared with the amount when that of Dumas was employed. A table of the results of 16 analyses is given, which shows that the deficit varied from about $\frac{1}{17}$th to about $\frac{1}{3}$rd of the total amount of nitrogen present.

C. E. G.

On the Relation between the Quantity of Starch contained in Potatoes and their Relative Density, and a new Table for calculating the Percentage of Starch contained in Potatoes from their Specific Gravity. By F. Heidepriem (*Landw. Versuchs.-Stat.*, xx, 1—19).—About thirty years ago, Berg and Lüdersdorf devised a method for the valuation of potatoes, founded upon the relation between the quantity of starch they contain and their density. This method was afterwards improved by Balling and Pohl, who compiled tables by means of which the percentage of starch could readily be found from the specific gravity. These tables are still extensively used in Germany for technical purposes. Two methods are in use for determining the specific gravity of the potatoes. The first consists in placing them in a concentrated solution of common salt, and then diluting until they just remain suspended in the liquid, when the specific gravity of the brine being taken by a hydrometer, gives also that of the potatoes. The other consists simply in weighing a given quantity first in air, and afterwards in water. This method is preferred, as the first does not give very trustworthy results. During the year 1875 the Agricultural Society of Cöthen carried out some experiments with potatoes, to ascertain which sorts were the richest in starch and the most productive. The analytical work necessary for this purpose was performed at the local Experimental Station, the starch being determined, not only by chemical analysis, but also indirectly from the specific gravity of the tubers, according to the tables of Balling and Pohl. As the results thus obtained were unsatisfactory, fresh experiments were undertaken to investigate the relation between the density of the tubers and the quantity of starch contained in them, and from the results of these experiments the following table has been drawn up:—

Table for Determining the Percentage of Starch and Dry Substance in Potatoes from the weight of 5 kilograms under Water.

Weight of 5 kilograms under water.	Starch per cent.	Dry substance per cent.	Weight of 5 kilograms under water.	Starch per cent.	Dry substance per cent.
630	25·07	32·29	455	15·97	23·19
625	24·81	32·03	450	15·71	22·93
620	24·55	31·77	445	15·45	22·37
615	24·29	31·51	440	15·19	22·41
610	24·03	31·25	435	14·93	22·15
605	23·77	30·99	430	14·67	21·89
600	23·51	30·73	425	14·41	21·63
595	23·25	30·47	420	14·15	21·37
590	22·99	30·21	415	13·89	21·11
585	22·73	29·95	410	13·63	20·85
580	22·45	29·69	405	13·37	20·59
575	22·21	29·43	400	13·11	20·33
570	21·95	29·17	395	12·85	20·07
565	21·69	28·91	390	12·60	19·82
560	21·43	28·65	385	12·34	19·55
555	21·17	28·39	380	12·08	19·30
550	20·91	28·13	375	11·82	19·03
545	20·65	27·87	370	11·56	18·78
540	20·39	27·61	365	11·30	18·55
535	20·13	27·35	360	11·04	18·26
530	19·87	27·09	355	10·78	18·00
525	19·61	26·83	350	10·52	17·73
520	19·35	26·57	345	10·26	17·48
515	19·09	26·31	340	10·00	17·22
510	18·83	26·05	335	9·74	16·96
505	18·57	25·79	330	9·48	16·71
500	18·31	25·53	325	9·21	16·43
495	18·05	25·27	320	8·95	16·17
490	17·79	25·01	315	8·69	15·91
485	17·53	24·75	310	8·43	15·65
480	17·27	24·49	305	8·17	15·39
475	17·01	24·23	300	7·91	15·13
470	16·75	23·97	295	7·65	14·87
465	16·49	23·71	290	7·39	14·61
460	16·23	23·45	285	7·13	14·35

H. H. B. S.

Technical Chemistry.

On the Action of Potassium Ferricyanide on Metallic Silver, and the Conversion of Silver Negatives. By J. M.

EDLER (*Chem. Centr.*, 1876, 569—570).—In the method of intensifying negatives with potassium ferricyanide and a lead or uranium salt, nothing has hitherto been known of the reactions which take place. To investigate the reasons of the intensifying, the author acted on freshly precipitated silver with a solution of potassium ferricyanide, and found the following reaction to take place:—

$$4K_3Fe(CN)_6 + 4Hg = 3K_4Fe(CN)_6 + Hg_4Fe(CN)_6.$$

When heat is applied, the mixture smells of hydrocyanic acid, and silver goes into solution. In presence of lead or uranium salts, lead or uranium ferrocyanide is formed:

$$3K_4Fe(CN)_6 + 6Pb(NO_3)_2 = 3Pb_2Fe(CN)_6 + 12KNO_3.$$

Ferric salts cause a precipitate of Prussian blue, and with ferricyanide, of Turnbull's blue in the negative; this occurs either on silver or platinum negatives. As 2 equivalents of silver precipitate 6 of lead or uranium as ferrocyanide, while only 1 atom of platinum is precipitated by 4 of silver, 1 of gold by 3 of silver, and 1 of mercury by 2 of silver, it is evident that a greater intensification may be produced by means of lead or uranium, than with these metals. W. R.

An Alkaline Iron Developing Liquid. By J. M. EDLER and V. TOTH (*Chem. Centr.*, 1876, 569).—Tartaric acid is added to excess of ammonia, potash, or soda, and poured into a solution of ferrous sulphate till the precipitate dissolves. The solution does not keep, but must be used at once. The reducing action is most energetic if potash be used instead of sodium carbonate or ammonia. W. R.

New Gold Bath. By DURAND (*Chem. Centr.*, 1876, 569).—Gold chloride, 1 gram; lime-water, 450 grams; sodium acetate, 12 grams. Heat the solution, and use it next day. The solution should be kept in a stoppered bottle, and mixed with four or five times its volume of water before use. W. R.

Preparation of Sulphur from Pyrites. By P. W. HOFMANN (*Chem. Centr.*, 1876, 187).—It is known that, in the preparation of sulphuric acid, the sulphur present in iron-pyrites is evolved in the form of sulphurous acid. By adding to the latter substances which possess a greater affinity for oxygen than sulphur, the sulphur can be separated from sulphurous acid. For instance, when sulphurous acid is passed over red-hot coal, sulphur distils over. This reaction gave unsatisfactory results when applied to larger quantities of the gas, and the author therefore thought it necessary to investigate the influence exerted by bodies of great affinity for oxygen on sulphurous acid under various conditions. He found that a whole series of substances which possess this property in a high degree can be obtained at any place, and are worked up again to their former conditions by means of cheap reducing agents. This group includes the sulphides of the alkalis and alkaline earths, which have hitherto been considered to have less affinity for oxygen than sulphur. The sulphides of potassium, sodium, calcium, and barium were subjected to special investigation. Judging from a practical point of view, sulphide of calcium seems the most suitable of these sulphides on account of its small atomic weight and its ready method of preparation. On passing sulphurous acid over sulphide of calcium heated to dull redness, the immediate change is absorption of the gas, provided that sufficient sulphide of calcium is present. After this sulphur distils over and the sulphide of calcium is converted into the sulphate, which may be brought back to its former state by passing common coal-gas over it, or heating it very strongly after addition of sufficient coal.

D. B.

Injurious Effects produced by covering Roads with Pyrites-residues. By T. SARRAZIN (*Arch. Pharm.* [3], ix, 418—422).—In consequence of the manufacture of sulphuric acid from pyrites at Nienburg, in Hanover, a considerable quantity of burnt residues accumulated, which, forming an excellent material for improving gravel or loam-pavings, was largely used in the neighbourhood. Analysis proved, however, that these residues contained not only sulphide of iron and earthy constituents, but also sulphide of zinc, and that by the influence of the oxygen of the atmosphere and the presence of water, these sulphides were gradually converted into the corresponding sulphates, which were continually extracted by the rain-water and thus entered the soil, giving rise to various injurious effects.

In a village near the above-mentioned spot, a farmer observed one morning that by adding his well water to new hot milk, the milk was curdled. By examining this water, oxide of iron and sulphate of zinc were detected, and, judging from the defective consistency of the wooden sides of the well, its low situation, and the fact that some time ago a shoot of pyrites-residues was thrown on the path running by the side of the farm-house, the presence of the above-mentioned constituents may be easily comprehended. At this place and in its vicinity various similar observations were made. Moreover, it was found that the growth of grass or corn ceased on fields, the paths of which were covered with these residues. D. B.

Use of the Ammonia-Soda Process in Working up Gas-liquors. By T. GERLACH (*Dingl. polyt. J.*, ccxxiii, 82—90).—The preparation of soda by means of ammonia is known to depend upon the fact, that by introducing carbonic acid gas into a concentrated solution of common salt, which is saturated to a certain degree with caustic ammonia, bicarbonate of sodium is separated on account of its inferior solubility, while sal-ammoniac remains in solution. The former, after filtering and washing, is converted into neutral carbonate of sodium by calcining the mass, while from the filtered solution containing undecomposed ammonium carbonate, sodium chloride and sal-ammoniac, caustic ammonia is recovered by distillation with lime. Experiments have shown that the decomposition takes place with equal readiness, if, in the place of common salt, other sodium salts are used, *e.g.*, Glauber's salt or Chili-saltpetre, in which cases sulphate or nitrate of ammonium remains in solution. In all cases the decomposition is only partial, not more than one-half of the soda salts used separating in the form of bicarbonate. It must be observed, however, that by this separation of bicarbonate, the solution is reduced in density and becomes capable of taking up a larger quantity of chloride nitrate or sulphate of sodium, whereby a further decomposition of the ammonium carbonate is effected; and by thus keeping the solution continually saturated with sodium chloride, as much as three-fourths of the total quantity of that salt may ultimately be converted into carbonate.

1. *Decomposition of Ammoniacal Distillation-products by means of Rock-salt or Sea-salt.*—A concentrated solution of ammonium carbonate is prepared by distilling gas-liquor, and chloride of sodium is added. The concentrated solution should contain 1 eq. of NaCl to 1 eq. of $(NH_4)_2CO_3$, having a specific gravity of 1·22. Carbonic acid is then passed into the mixture, until it no longer separates the bicarbonate of sodium. The latter is separated from the liquid, washed, and heated or boiled with water until a concentrated soda-solution is formed, which is left to crystallise out. The carbonic acid escaping may be used for decomposing a fresh quantity of liquor. The filtrate from the sodium bicarbonate is distilled, in order to obtain the ammonium carbonate, and from the liquid, which now contains only sal-ammoniac and sodium chloride, the former is obtained by crystallisation, after the latter has been separated from the hot liquor by concentration. The liquor may also be distilled with lime, in order to prepare ammonia.

The following are the differences between the author's method and the ammonia-soda process:—(1.) It is more effectual, fresh quantities of gas-liquor being continually worked up; whereas the ammonia process results merely in the preparation of sodium carbonate, the sal-ammoniac taken being used in the form of caustic ammonia for the next operation. (2.) The sal-ammoniac formed by decomposing gas-liquor with common salt is obtained in the crystalline form, instead of being decomposed by lime and used as caustic ammonia for another operation; so that there is no loss of ammonia by volatilisation. (3.) No lime is required, excepting the very small quantity which is necessary to decompose the non-volatile ammonium compounds present in gas-liquor. (4.) No loss of salt is sustained, as it is used for the next operation. For each equivalent of sodium chloride, therefore, 1 eq. of soda is obtained as bye-product, a yield which the ammonia-process has not yet been able to furnish. (5.) The carbonic acid contained in gas-liquor is utilised as ammonium carbonate, whereas in the ammonia-process caustic ammonia—or sal-ammoniac decomposed by lime—is formed. (6.) With the exception of the gas-liquor, which is distilled off, no useless bye-product is obtained. (7.) The costs for recovering the ammonia are saved, as the sal-ammoniac liquors do not require much concentration in order to deposit sal-ammoniac. (8.) By continually using fresh quantities of gas-liquor, the production of sal-ammoniac goes hand in hand with the preparation of a saleable bye-product, viz.:—

2. *Decomposition of Ammoniacal Distillation-products by means of Glauber's Salt.*—A concentrated solution of ammonium carbonate is

again prepared and treated with Glauber's salt. The solution should contain 1 eq. $(NH_4)_2CO_3$ to 1 eq. Na_2SO_4, and have a sp. gr. of 1·30. The further treatment for separating the carbonate of sodium, sulphate of ammonium, and sulphate of sodium, is similar to that described under (1).

3. *Decomposition of Ammoniacal Distillation-products by means of Chili-saltpetre.*—A concentrated solution of equivalent quantities of $(NH_4)_2CO_3$ and $NaNO_3$ having a sp. gr. of 1·37 is prepared and treated like the former. The end-products are nitrate of ammonium and carbonate of sodium.

In all cases the cooled gases of coke fires or of lime-kilns can be used as carbonic acid, while the apparatus used in the ammonia-soda process are also best suitable for decomposing the ammoniacal distillation-products by means of the above-mentioned alkali salts.

A comparison of the working expenses and profits of the old and new processes shows that the latter yields a considerably greater profit than the former.

4. *Separation of Sal-ammoniac and Common Salt.*—On evaporating a solution of equal quantities of sal-ammoniac and common salt, the latter crystallises out mixed with sodium chloride. If, however, the solution is further concentrated, sodium chloride separates from the hot solution. Since the latter is always mixed with sal-ammoniac, it is added to a fresh quantity of distillation-products in order to be decomposed by carbonic acid.

By the following method of systematic evaporation, the author separates the sodium chloride as completely as possible from the chloride of ammonium. Four boilers are placed side by side in a row, and only one of them, say the left end boiler (IV), is filled with fresh liquor. The salt separating from this boiler is taken out, while that from III is transferred to IV; that from II to III, and that from I to II. On the other hand, the liquor in boiler I only is taken out, while that in II is transferred to I, that in III to II, and that in IV to III. The liquor in all the boilers is kept at the same height during the whole operation. The boiling points of the liquors in I and II were 116°, in III, 112°, and in IV, 108°. The sal-ammoniac obtained gave, after ignition, a residue of 1·75 p. c. of NaCl.

5. *Separation of Sulphate of Ammonium from Sulphate of Sodium.*—From a solution of the equivalent quantities of $(NH_4)_2SO_4$ and Na_2SO_4, a double salt is obtained, having the following formula:—

	NH_4OSO_3.	+	$NaOSO_3$.	+	$2HO$	or	$(NH_4NaSO_4 + H_2O)$.
	66		71		18	=	155
Crystallised..	42·58		45·81		11·61	=	100
Anhydrous...	48·18		51·82		—	=	100

But by evaporating the solution, anhydrous Glauber's salt is separated, while sulphate of ammonium remains in solution.

The separation is effected by means of the same arrangement of boilers as described in the former instance. The liquor in I and II has a boiling point of 111°, that in III, 110°, and that in IV, 106°. The liquor in I crystallises on cooling, forming perfectly white sulphate of ammonium, containing only 1·8 per cent. of Glauber's salt, while the anhydrous Glauber's salt containing about 20 per cent. of sulphate of ammonium is used with fresh portions of Glauber's salt, in order to decompose the next lot of ammoniacal distillation-products.

In conclusion, it is noteworthy that in crystallising common salt or anhydrous Glauber's salt at the boiling heat, these salts are liable to be burnt. It is necessary, therefore, to evaporate the liquors in double-jacketed steam-boilers, provided with steam worms to facilitate the evaporation. D. B.

Manufacture of Aluminium Sulphate, Gelatinous Silica, and Calcium Chloride from Blast-furnace Slags. By AMENE, C. KIANDT, FABRI, and MILIUS (*Chem. Centr.*, 1876, 491).—The slag is treated with hydrochloric acid in a peculiar apparatus, the acid being condensed in vessels of sandstone. The acid solution is diluted, the silica allowed to settle, and the aluminium precipitated as hydrate by calcium carbonate in impalpable powder. This operation requires care, for no iron must be precipitated. The washed and dried precipitate is converted into sulphate with boiling sulphuric acid. The gelatinous silica is washed and dried and the solution of calcium chloride evaporated to dryness. W. R.

Recovery of Tin from Scraps of Tinned Iron. By LAROCQUE (*Chem. Centr.*, 1876, 591).—The scraps are mixed with fine wood charcoal and ½ p. c. of salt, and heated in an apparatus, the middle of which is provided with a sort of sieve. The upper part of the vessel is heated to redness while the lower portion is cooled with water. The tin melts and runs through the holes of the sieve. W. R.

Use of Palladium instead of Silver in Electro-deposition. By FRANTZ (*Chem. Centr.*, 1876, 592).—The palladium is precipitated with mercuric cyanide; and the cyanide is mixed with 7 p. c. of potassium ferrocyanide, 3 p. c. of caustic potash, and 60 p. c. of water, and boiled for half an hour, the evaporated water being replaced. This bath is useful for palladinizing metallic objects, previous coating with silver being unnecessary. W. R.

Effect of Hot Air on the Blast-furnace Process. By LEDEBUR (*Chem. Centr.*, 1876, 151).—From his minute accounts on this subject the author draws the following conclusion:—The relative saving of fuel by hot air is generally greater when small furnaces are employed and difficultly reducible ores are worked off, as with the former less of the heat evolved during the combustion is used up, and a larger quantity of it carried off by the flue-gases, while with the latter a direct reduction, and therefore consumption, of heat results, which is covered most profitably by the introduction of hot air and not by the increase of fuel. D. B.

Nomenclature for Iron and Steel. (*Dingl. polyt. J.*, ccxxiii, 325).—From the following circumstances an international commission was formed at last year's exhibition in Philadelphia in order to constitute a uniform nomenclature for iron products:—(1.) The name "steel," which is given to certain qualities of soft iron occurring in commerce, does not distinguish them sufficiently well from the substance which was hitherto called steel, characterised by its hardening and tempering properties. (2.) A nomenclature recognised by chemists in all languages is needed for commerce as well as for science, especially as actions at law are already in progress, the decision of which depends upon the manner in which the name "steel" is explained. (3.) Although the uniformity obtained by melting is very generally recognised as the special characteristic of hard and soft steel, this uniformity may also be expressed by other names, while the old name "steel" is not retained for all malleable iron products which admit of hardening and tempering. This commission recommends the following nomenclature:—(1.) All malleable compounds of iron with the ordinary ingredients, which have been prepared from softened masses or faggots, or in any form other than the liquid state, and which cannot be hardened or tempered, and are similar to the substance called wrought-iron, are for the future to be called "weld-iron" (*Schweisseisen*, *fer soudé*, *wälljern*). (2.) Compounds of the previously described quality which from any cause are capable of being hardened and tempered, and therefore are similar to the product hitherto called "puddled steel," are in future to be called "weld-steel" (*Schweissstahl*, *acier soudé*, *wallstäl*). (3.) All compounds of iron with the ordinary ingredients which have been cast in the liquid state to malleable masses and cannot be appreciably hardened when placed in water whilst red-hot, are to be called "ingot-iron" (*Flusseisen*, *fer fondu*, *götjern*). (4.) All compounds of the last-described quality, which from any cause are capable of being tempered, are to be called "ingot-steel" (*Flüssstahl*, *acier fondu*, *götstäl*). D. B.

Manufacture of Rails from Iron containing Phosphorus. (*Chem. Centr.*, 1876, 509).—The process, as carried out at the Ferre-Noire Works near St. Etienne, although not yet perfected, promises good results.

A white iron (not steel) is produced by melting pig-iron with old rails,—both irons must be poor in silicon,—removing the impurities by oxidation, and reducing oxidised iron by the use of an alloy of iron and manganese containing from 40 to 60 per cent. of the latter metal. Almost the whole of the carbon is then removed, and a product is obtained which makes excellent rails. M. M. P. M.

Products obtained by Calcining in close vessels the Residues obtained in the Fermentation of Beet-root Molasses. By CAMILLE VINCENT (*Compt. rend.*, lxxxiv, 214—217).—In the manufacture of alcohol from beet-root molasses a residual liquor is obtained known as "les vinasses," which is evaporated and calcined for the sake of the saline constituents which it contains. By calcining the concentrated liquor in a close vessel instead of in an open furnace four products are obtained: an amber-coloured watery distillate, tar, gas, and a porous charcoal containing salts of potash and soda.

The watery portion is strongly alkaline and contains ammonium carbonate, sulphydrate, and cyanide; when it is treated with sulphuric acid in excess, and submitted to fractional distillation, a complex liquid comes over containing, besides hydrocyanic acid and some undetermined substances, methyl sulphide, methyl cyanide, and methyl alcohol. By rectifying this distillate first over ferrous hydrate and quick-lime, and secondly with a little sulphuric acid, tolerably pure methyl alcohol is obtained, the yield from a given weight of molasses being considerably larger than that obtained from the same weight of wood in the usual process of destructive distillation.

The latter portions of the crude distillate were acid. By suitable treatment the following acids were isolated in a state of sufficient purity to enable them to be recognised:—Formic, acetic, proprionic, butyric, valeric, and caproic acids.

The mother-liquors from the ammonium sulphate, which always refuse to crystallise, were found to contain a very considerable quantity of trimethylamine sulphate; the alkaloïd was liberated by means of soda, collected in hydrochloric acid, and an abundant crystallisation of trimethylamine hydrochloride thus obtained.

The tar was examined by submitting it to distillation; in this way an ammoniacal and oily distillate was obtained, the former containing ammonium carbonate and sulphydrate. From the oily portion a small quantity of phenol was isolated, but no benzene or toluene could be detected.

The gaseous products were also analysed, and consisted of hydrogen, marsh-gas, carbon monoxide, and carbon dioxide. J. W.

Method of Extracting and Purifying Sugar. By TANNEVAN (*Chem. Centr.*, 1876, 591).—The juice is treated with oak-bark, gall-nuts, or catechu, till it has an acid reaction and then boiled; to the filtered liquid a decoction of oak-bark is added to saturate the alkalis. The separation with lime, saturation, and treatment with oak-bark is again repeated. The yield of crystalline sugar is said to be greater, and that of molasses less, than by the usual processes. W. R.

Artificial Laurel Water. By A. RIPPING (*Arch. Pharm.* [3], ix, 526—531).—By the differences which are observed in laurel waters brought into the market, the author was led to suppose that some artificial laurel waters exhibit the reactions usually regarded as characteristic of the natural water; moreover, as he succeeded in preparing an artificial laurel water, he endeavoured to find out other tests by which laurel water so prepared may be distinguished from the natural water.

In order to prepare the artificial water, it was in the first place requisite to estimate the quantity of oil in distilled laurel water. Half a liter was neutralised with pure potash lye, the mixture shaken up with ether, and after evaporation of the ether at the ordinary temperature, the oil was dried in a desiccator for 48 hours and weighed. 3 g. of oil were obtained for 1 liter. In the next place hydrocyanic acid was prepared. For this purpose an improved form of Fleischer's apparatus for determining ammonia was used. 50 parts of yellow prussiate of potash were brought into a flask of 2 c.cm. capacity, and 35 parts of concentrated sulphuric acid added, the flask being then connected with the rest of the apparatus. 15 g. of prussiate of potash yielded 10 c.cm. of hydrocyanic acid. After having made the strength of the acid the same as that of laurel water, 1 liter was treated with 3 g. of oil of bitter almonds. The artificial water was found to correspond with the ordinary reactions for natural water, its composition being the same as that of natural laurel water after the lapse of about eight weeks. 10 c.cm. required 5 c.cm. of normal silver solution. Mixed with $\frac{1}{3}$ vol. of ammonia, it formed a distinct opalescence after 10 minutes, and became quite non-transparent after 20 minutes.

Mohr gives a reaction for distinguishing artificial and natural water of bitter almonds, depending on the fact that nitrate of silver yields a slight opalescence with the natural water, and after further addition of nitric acid and ammonia, a copious precipitate. The author has also observed a difference in the behaviour of artificial and natural laurel water with nitrate of silver. In natural distilled water, the hydrocyanic acid is totally fixed as benzaldehyde, the turbidity being due to the presence of cyanide of ammonium formed during the distillation, aqueous prussic acid yielding formic acid and ammonia when warmed. One part of the latter yields with the hydride of benzyl, benzyhydramide, while another part yields cyanide of ammonium. However, it had to be determined whether by a second distillation, or by some other means, artificial laurel water could yield a compound consisting of benzaldehyde and hydrocyanic acid. The following accounts are given:—(1.) Distillation yields a liquid which soon turns brown and becomes unfit for use. (2.) By distilling with prussiate of potash, sulphuric acid, and oil of bitter-almonds, a distillate is obtained, which is almost free from benzaldehyde. The acid used must be diluted with twice its own weight of water, otherwise the distillate will be adulterated with hydroferrocyanic acid. (3.) 1·5 g. of oil of bitter-almonds was mixed with $\frac{1}{2}$ liter of distilled water, 14 g. of cyanide of potassium added, and the mixture treated with 6 g. of previously diluted sulphuric acid. The quantity of acid was calculated accurately for forming the neutral sulphate. Although the distillation commenced on a water-bath, the oil being dissolved in the water, and every molecule of hydrocyanic acid being enabled to act on the benzaldehyde as quickly as it was formed, no compound could be obtained, the distillate consisting exclusively of dilute hydrocyanic acid, so that in this case also the oil was retained by the sulphuric acid. (4.) 6 g. of oil of bitter almonds were mixed with $\frac{1}{2}$ liter of distilled water, the mixture placed in a tubulated retort, and treated with 4·5 g. of cyanide of potassium. Carbonic acid gas was then introduced, which resulted in the decomposition of the cyanide of potassium, hydrocyanic acid being the product formed. The result was quite different from the former, benzaldehyde distilling over, combined with hydrocyanic acid, leaving bicarbonate of potassium and benzoïn in the retort. The smell of the water obtained was, however, very different from that of aqua laurocerasi. Another experiment was undertaken with real laurel oil, and the process conducted similarly to the former, excepting that the distillation was carried on over a gas flame, and the retort connected with a Liebig's condenser. In this case an artificial laurel water was obtained, which corresponded with the natural water in all its properties.

It was perfectly free from formic acid, and contained a larger or smaller quantity of cyanide of ammonium.

The oils used for the preparation of artificial water are easily distinguished from one another. Oil of bitter almonds gives crystals when placed on a watch-glass covered with a bell-jar, and left at rest for 14 days, while laurocerasus oil does not give the slightest indications of crystals. Nitrobenzene is recognised by the following test. The water is shaken up with chloroform, the latter evaporated off, the residue treated with alcohol and water, and exposed to the action of zinc and hydrochloric acid. If after the addition of chlorate of potassium a change of colour is obtained, nitrobenzene is present, the aniline formed by treatment with zinc and hydrochloric acid being converted by the chlorate of potassium into rosaniline, which dissolves in the alcoholic liquid with a red colour. D. B.

Wool and Cloth Dyed Green with Picric Acid. By J. HAUSNER (*Dingl. polyt. J.*, ccxxiii, 107).—In order to test grass-green military cloths as to their permanency, sample cuttings are treated with dilute hydrochloric acid of 1·0007 sp. gr.; also with dilute alcohol of 0·9714 sp. gr., at 75°. Most cloths stand the alcohol test, but are altered by hydrochloric acid, the cloth and liquid turning blue, a property which shows that the hydrochloric acid test depends chiefly on the blue contained in the green. Hydrochloric acid is coloured blue by sulphate of indigo and by aniline-blue, but is not altered by vat-blue. It is easy to understand that dyers prefer to obtain light shades by using a more certain and simple method than the vat-process, and it may also be supposed that, on the same grounds, the green dyeing by means of picric acid has mostly been combined with the modern methods of blue-dyeing. A series of experiments showed, however, that vat-blue woollen stuffs dyed green with a weak alcoholic picric acid solution remained unattacked by alcohol and hydrochloric acid, and were quite permanent after long exposure to the sun and rain. D. B.

Chrysoïdin. By O. N. WITT (*Deut. Chem. Ges. Ber.*, x, 350). The author claims to have prepared chrysoïdin in January, 1876, and he states that its commercial production was regularly carried on near London, by April, 1876. R. R.

Use of Alkaline Sulphides in Leather-dressing. By A. GÉLIS (*J. Pharm. Chim.* [4], xxiv, 218—221).—The employment of alkaline sulphides, especially sodium sulphide, for the removal of the hair from hides, has recently been published by Eitner, of Vienna, as a new invention, and has been commended in a number of German journals. The object of this paper is to draw attention to the fact that the same process was patented in France in 1838, by Boudet and Domingue.

H. H. B. S.

Bleaching of Raw Eggermoth Silk and other so called Wild Silks. (*Chem. Centr.*, 1876, 509).—In Tessié du Motay's patent process the silk is immersed for 15 minutes in a 2 per cent.

solution of permanganate, then in a solution of sulphurous acid, then in sulphuretted hydrogen, and, after working again, in sulphurous acid. M. M. P. M.

Improvements in the Manufacture of Varnish. By ZINGLER (*Chem. Centr.*, 1876, 591, 592).—A mixture of 1 pt. of carbon disulphide, 1 pt. of camphene or turpentine, 1 pt. of benzin or rectified petroleum, and 2 pts. of wood spirit, are heated in a close vessel, and powdered copal or other resin added to the solvent in the proportion of 106 : 125 per 50 kilos. of resin. The mixture is allowed to stand for some days, and then a fatty oil is added. W. R.

Prevention of Boiler Incrustations. (*Dingl. polyt. J.*, ccxxiii, 327).—The influence which the formation of boiler deposits exercises on the consumption of coal is illustrated by Kolb, who states that a boiler in Amiens, which, when clean, gave for 1 kilo. coal 7·5 kilos. steam, gave only 6·4 kilos. after the lapse of two months, showing a decrease of 17 per cent. Kolb recommends, as the best means of purifying boiler water, to use caustic soda, which is supposed to react with the calcium bicarbonate, forming sodium carbonate, separating calcium carbonate and precipitating the gypsum. If the water to be purified were always to contain the same number of equivalents of lime as bicarbonate and as gypsum, this statement would be correct. D. B.

New Applications of Glycerin in the Laboratory. By A. H. CHURCH (*Chem. News*, xxxv, 1).—Pure glycerin smeared on the inlet pipes of Bunsen burners, &c., prevents the adhesion of the india-rubber tubing: if the cement used to fix the metal burner of paraffin lamps to the glass reservoir be soaked with glycerin before introducing the oil, the disagreeable leakage of the oil at the joint will be prevented. E. W. P.

Preservation of Wood. By O. KRUG (*Chem. Centr.*, 1876, 15).—The process is chiefly dependent upon a peculiar arrangement of a series of iron vessels one within the other, whereby the impregnating liquid (sodium creosote) is caused to act more rapidly and more thoroughly upon the wood which is to be preserved. M. M. P. M.

Renewal of Old Corks. (*Dingl. polyt. J.*, ccxxii, 190).—Mohr recommends that the corks be collected and soaked in hot water. The following day they are washed repeatedly with pure water and soaked in a mixture of 15 parts of hot water and 1 part of hydrochloric acid. After a few hours they are taken out of this bath, washed well and dried; they then exhibit the appearance of new cork. D. B.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XVI.—*Action of Solutions of Alkaline Oxalates on the Earthy Carbonates and of Solutions of Alkaline Carbonates on the Earthy Oxalates.*

By WATSON SMITH.

ON one occasion my attention was drawn to the fact that a solution of ammonium oxalate brought into contact with chalk or powdered marble, was almost instantly attacked, even in the cold; and on heating, an ammoniacal odour at once became apparent; whilst on boiling it became quite strong. Sodium oxalate was also tried, with similar results as regards alkaline reaction. A quantity of perfectly neutral sodium oxalate was dissolved in water, and into the cold solution some powdered marble was added, and the whole shaken. Immediately the solution showed an alkaline reaction to litmus, and on warming, filtering, and adding hydrochloric acid to the filtrate, a very distinct effervescence was observed. It now appeared interesting to attempt the measurement of the extent of this reaction, and to compare it with that ensuing between the alkaline carbonates and earthy oxalates.

I. *Action of Sodium Oxalate in Solution on Calcium Carbonate.*

Equivalent weights.—1. *Cold.* 6·7 grams of sodium oxalate with 5 grams of calcium carbonate (powdered marble), and 250 c.c. cold water, were let stand, with occasional shaking, for three hours, then filtered and washed with about 50 c.c. more water till no more alkaline, and determined the sodium carbonate by means of standard acid. In two independent experiments—(1) 1·049 gram Na_2CO_3, (2) 1·053 gram Na_2CO_3, mean = 1·051 Na_2CO_3, were formed from the 6·7 grams of sodium oxalate taken, in which the sodium is equivalent to 5·3 grams of sodium carbonate. Hence out of a possible 5·3 grams 1·051 gram of Na_2CO_3 was formed = 19·83 per cent.

2. *Hot.* 6·7 grams of sodium oxalate with 5 grams of calcium carbonate gave, on boiling for three hours, with 250 c.c. water, filtering, boiling hot, and washing with enough hot water to leave unalkaline residue.

Filtrate, in two experiments—(1) 1·2179 grm. Na_2CO_3, (2) 1·2090 grm. Na_2CO_3, mean = 1·2135 Na_2CO_3, was formed from the 6·7 grams of sodium oxalate taken, in which the sodium is equivalent to 5·3 grams of Na_2CO_3.

Hence out of a possible 5·3 grams, 1·2135 grm. Na_2CO_3 was formed = 22·90 per cent.

When the residue left on the filter was treated with more sodium oxalate, the same reaction repeated itself, apparently with the same activity. It should therefore be possible to exhaust the whole of the calcium carbonate by repeated treatment with sodium oxalate solution.

II. *Action of Sodium Carbonate Solution on Calcium Oxalate.*

Equivalent weights.—1. *Cold.* 5 grams of sodium carbonate were treated with 6·04 of calcium oxalate, the carbonate being dissolved in 250 c.c. of water. The solution was left, with occasional shaking, from four to five hours, then filtered, and washed as before with about 50 c.c. water, till it was no more alkaline.

5 grams of sodium carbonate would require	56·24	c.c. standard acid.
Filtrate actually required	47·20	„ „
	9·04	„ „

9·04 c.c. acid are equivalent to 0·8037 grm. Na_2CO_3.

$\frac{100 \times 0 \cdot 8037}{5}$ = 16·07 per cent. of possible conversion of Na_2CO_3 into $Na_2C_2O_4$.

2. *Hot.* Above proportions boiled for half an hour; let stand, filtered cold, and washed with hot water till no more alkaline.

5 grams of sodium carbonate would require	56·24	c.c. acid.
Filtrate actually required	26·80	„ „
	29·44	„ „

29·44 c.c. acid are equivalent to 2·617 grams of Na_2CO_3.

$\frac{100 \times 2 \cdot 617}{5}$ = 52·34 per cent. of possible conversion of Na_2CO_3 into $Na_2C_2O_4$.

III. *Action of Sodium Oxalate Solution on Calcium Carbonate (Powdered Marble).*

Double equivalent of Sodium Oxalate.—1. *Cold.* 5 grams of calcium carbonate were treated with a solution of 13·5 grams of oxalic acid exactly neutralised with soda, and the whole was made up to 250 c.c. with water, and left for 4¼ hours. Filtered, washed as before, but requiring double the quantity of wash-water; soda estimated in the filtrate. The quantity of sodium oxalate employed was a little *more* than a double equivalent.

The sodium, combined with 13·5 grams of oxalic acid, is equivalent to 11·36 grams of Na_2CO_3. We will suppose that the equivalent, or 6·7 grams of sodium oxalate ($Na_2C_2O_4$) [equivalent to 5·3 grms. of Na_2CO_3] acts directly on the $CaCO_3$, the balance or excess of the oxalate producing an effect which might be regarded as analogous to that of pressure or mass. Calculating on this assumption, we will reckon the action still on the equivalent to 5 grms. $CaCO_3$, or 6·7 grms. $Na_2C_2O_4$, the sodium in which is equivalent to 5·3 grms. Na_2CO_3. Sodium carbonate found in filtrate = 1·1113 gram.

Hence out of a possible 5·3 grams of Na_2CO_3, 1·1113 gram was formed = 20·97 per cent.; on boiling for some hours and filtering hot = 26·00 per cent.

Sodium Oxalate Solution on Calcium Carbonate.

Thus, other circumstances remaining the same, the reactions in the cold and hot, and also using excess of sodium oxalate, cold and hot, were as follows:—

		Action converting oxalate to carbonate.
I. Equivalent weights.	Cold	19·83 per cent.
” ”	Hot	22·90 ”
III. Excess of oxalate.	Cold	20·97 ”
” ”	Hot	26·00 ”

Sodium Carbonate Solution on Calcium Oxalate.

		Action converting sodium carbonate to oxalate.
II. Equivalent weights.	Cold	16·07 per cent.
” ”	Hot	52·34 ”
(Let stand 4—5 hours, with shaking.)		
IV. Excess of sodium carbonate, double equivalent	Cold....	13·09 ”
” ”	Hot	78·35 ”
(Left for 2 hours, with shaking.)		

V. The experiment was now tried of treating the same portion of *calcium carbonate* with successive quantities of sodium oxalate (total used 33·5 grams), using the same quantity of water on each occasion and boiling. The results were as follows:—

(1.) 22·90 per cent. action converting oxalate to carbonate.
(2.) 8·05 „ „ „
(3.) 8·05 „ „ „
(4.) 5·03 „ „ „
(5.) 1·84 „ „ „

45·87 total.

The action diminishes, and finally almost ceases, in all probability owing to an enveloping coat of calcium oxalate being formed over the particles of marble, and also to the reduction of surface by the wearing down of the superficial inequalities.

VI. A solution of 5·3 grams of sodium carbonate (Na_2CO_3) was now boiled with 6·40 grams of calcium oxalate (equivalents), the volumes of water used being the same as in V.

By titrating the filtrate with standard sulphuric acid, the amount of sodium carbonate undecomposed by calcium oxalate was ascertained, and by subtracting from the total weight taken the amount converted into oxalate. The residue was then treated with a fresh weight of 5·3 grms. Na_2CO_3, boiled, lixiviated, filtered, and again titrated; this was three times done. Results as follows :—

		Sodium carbonate converted to oxalate.
(1.) 3·424 grms. Na_2CO_3 converted	=	64·60 per cent.
(2.) 1·139 „ „	=	21·50 „
(3.) 0·410 „ „	=	7·73 „
Total		93·83

Hence by three boilings and lixiviations as above, the 6·40 grams of calcium oxalate were almost wholly converted into carbonate, altogether 15·9 grams of sodium carbonate being required.

I. *Action of Sodium Oxalate on Strontium Carbonate.*

Equivalent weights.—1. *Cold.* 6·7 grams of sodium oxalate with 7·375 grams of strontium carbonate and 250 c.c. cold water were let stand with occasional vigorous shaking for 3—4 hours. Filtered, washed, and determined the sodium carbonate as before by standard acid :—

$$\left.\begin{array}{ll}(1.) & 0{\cdot}4001\\ (2.) & 0{\cdot}4089\end{array}\right\}\text{Mean} = 0{\cdot}4045 \text{ gram } Na_2CO_3.$$

Hence out of a possible 5·3 grams of Na_2CO_3, 0·4045 gram was formed = 7·63 per cent.

2. *Hot.* The above proportions were now again taken and boiled, filtered hot, washed, &c., as before :—

$$\left.\begin{array}{ll}(1.) & 0{\cdot}4045\\(2.) & 0{\cdot}4045\end{array}\right\}\text{Mean} = 0{\cdot}4045 \text{ gram } Na_2CO_3.$$

but of a possible 5·3 grams Na_2CO_3, 0·4045 gram was formed = 7·63 per cent.

II. *Action of Sodium Carbonate on Strontium Oxalate.*

1. *Cold. Equivalent weights* treated as in I, with cold water, frequently shaken, filtered, and washed.

57·24 per cent. sodium carbonate converted to sodium oxalate of what might have been, or of whole convertible amount.

2. *Hot.* Boiled for one hour, filtered, and washed till no more alkaline, as before.

79·96 per cent. sodium carbonate converted to oxalate, of whole convertible amount.

I. *Action of Sodium Oxalate on Barium Carbonate.*

Equivalent weights.—1. *Cold.* 6·7 grams of sodium oxalate were treated with 9·85 grams of barium carbonate and water as before—

$$\left.\begin{array}{ll}(1.) & 0{\cdot}2567\\(2.) & 0{\cdot}2567\end{array}\right\}\text{Mean} = 0{\cdot}2567 \text{ grm. } Na_2CO_3.$$

Hence out of a possible 5·3 grams Na_2CO_3, 0·2567 grm. Na_2CO_3 was formed = 4·84 per cent.

2. *Hot.* Above proportions again taken, but the lixiviation carried on at the boiling temperature.

Action increased very little, next to nothing = 4·97 to 5·00 per cent.

II. *Action of Sodium Carbonate on Barium Oxalate.*

Equivalent weights.—2. *Hot.* Treated as before.

2·65 grams Na_2CO_3, left undecomposed 0·3186 gram = 87·96 per cent. sodium carbonate converted to oxalate, of the carbonate taken.

1. *Cold.*—2·65 grams Na_2CO_3 left 0·7080 grm. undecomposed by the oxalate = 73·20 per cent. of the carbonate taken.

Some experiments were now made to ascertain the action of *ammonium oxalate* in solution on *calcium carbonate.*

Equivalent weights.—*Cold.* 3·1 grams of ammonium oxalate with 5 grams of calcium carbonate.

3·1 grams ammonium oxalate are equivalent to 6·7 grams of sodium oxalate = 5·3 grams of Na_2CO_3. Ammonium carbonate formed equivalent to *sodium carbonate* = 0·6505 gram.

$$\frac{100 \times 0{\cdot}6505}{5{\cdot}3} = 12{\cdot}27 \text{ per cent.}$$

Using a double equivalent of *ammonium oxalate:* 6·2 grams ammonium oxalate to 5 grams of calcium carbonate. Ammonium carbonate was formed equivalent to 0·717 grm. sodium carbonate—

$$\frac{100 \times 0{\cdot}717}{5{\cdot}3} = 13{\cdot}53 \text{ per cent.}$$

Using a double equivalent of *calcium carbonate:* 3·1 grams ammonium oxalate to 10 grams of calcium carbonate. Ammonium carbonate was formed equivalent to 1·027 gram of sodium carbonate—

$$\frac{100 \times 1{\cdot}027}{5{\cdot}3} = 19{\cdot}94 \text{ per cent.}$$

I. *Action of Sodium Oxalate on Lead Carbonate.*

Equivalent weights.—1. *Cold.* 6·7 grams of sodium oxalate with 13·35 grams of lead carbonate.

0·3363 grm. Na_2CO_3 formed—

$\frac{100 \times 0{\cdot}3363}{5{\cdot}30} = 6{\cdot}35$ per cent. sodium carbonate, formed, of what was present as sodium oxalate.

2. *Hot.*—Same proportions as above, but using boiling water.

0·6934 gram Na_2CO_3 formed—

$\frac{100 \times 0{\cdot}6934}{5{\cdot}30} = 13{\cdot}08$ per cent. sodium carbonate formed.

II. *Action of Sodium Carbonate on Lead Oxalate.*

Equivalent weights.—1. *Cold.* 7·375 grms. PbC_2O_4 with 2·65 grms. Na_2CO_3 =

$$\begin{array}{l} 2{\cdot}650 \\ 0{\cdot}489 \text{ grm. } Na_2CO_3 \text{ left undecomposed.} \\ \hline 2{\cdot}161 \text{ grms. } Na_2CO_3 \text{ converted into oxalate.} \end{array}$$

$\frac{100 \times 2{\cdot}161}{2{\cdot}65} = 81{\cdot}54$ per cent. sodium carbonate converted to oxalate.

2. *Hot.*

$$\begin{array}{l} 2{\cdot}6500 \\ 0{\cdot}2489 \\ \hline 2{\cdot}4011 \text{ grms. } Na_2CO_3 \text{ converted into oxalate.} \end{array}$$

$\frac{100 \times 2{\cdot}4011}{2{\cdot}65} = 90{\cdot}61$ per cent. sodium carbonate converted to oxalate.

The following table will show the comparative results obtained by causing equivalent weights of the afore-named salts to act upon one another, under the same conditions. The results are reckoned in terms of sodium carbonate (Na_2CO_3) as before stated:—

Action of Sodium Oxalate on the Earthy Carbonates.

Percentage of Na_2CO_3 formed of total possible.

	Cold.	Hot.
Calcium	19·83	22·90
Strontium	7·63	7·63
Barium	4·84	4·98
Lead	6·35	13·08

Action of Earthy Oxalates on Sodium Carbonate.

Percentage of Na_2CO_3 converted into oxalate of total possible.

	Cold.	Hot.
Calcium	16·07	52·34
Strontium	57·24	79·96
Barium	73·20	87·96
Lead	81·54	90·61

It will be observed that, *in the cold*, calcium carbonate is approximately as much more acted on than barium carbonate by *sodium oxalate solution*, as barium oxalate is than calcium oxalate by *sodium carbonate solution*. It is also noteworthy that in the action of the sodium oxalate solutions on the earthy carbonates, the increased effect by heat is slight, in the case of strontium, absolutely *nil*; in the case of lime greatest. When calcium oxalate is treated in the cold with sodium carbonate, no great action takes place, but on boiling the decomposition is increased somewhat over threefold. On reference to page 247, it will further be observed that though with an excess (double equiv.) of sodium carbonate in the cold, no increased action occurs, yet on boiling it is immensely increased, viz., sixfold.

XVII.—*Note on Thallious Platinocyanide.*

By R. J. Friswell and A. J. Greenaway.

In the year 1871 one of us had the honour of laying before the Society a paper describing a compound of thallious platinocyanide with thallious carbonate. The body in question forms dark red crystals, which reflect a green metallic light, and yield on analysis numbers leading to the formula, $Tl_2PtCy_4CO_3Tl_2$. In the same paper it was further stated that on treating the above salt with warm nitric acid and recrystallising the insoluble residue from water, colourless crystals were obtained, which gave on analysis numbers agreeing well with those required by the formula, Tl_2PtCy_4.

We have since found that Carstanjen had given* in 1867 the following method for the preparation of thallious platinocyanide:—"I neutralised hydroplatinocyanic acid, concentrated by careful evaporation, with thallious carbonate. . . . . I obtained from the spontaneously evaporated liquid blood-red needles, of PtCyTlCy. The crystals show by reflected light a splendid metallic green surface iridescence."

As these results are not in accordance with those obtained by one of us, and as no analysis is given by Carstanjen, we determined to re-investigate the subject, the more particularly as Carstanjen's is the only description of a platinocyanide of thallium we have been able to discover.

1st. Hydroplatinocyanic acid was prepared by dissolving platinous chloride in potassic cyanide, dissolving the resulting crystals in water, and precipitating the cupric platinocyanide by the addition of cupric sulphate. The cupric salt was carefully washed, and then boiled, with excess of baric hydrate, and the solution filtered from cupric oxide, raised to the boiling point, and a current of carbonic anhydride passed through it. It was then filtered from baric carbonate, and baric platinocyanide crystallised. The crystals of the latter were dissolved in water, and dilute sulphuric acid cautiously added to the boiling solution as long as a precipitate of baric sulphate was occasioned; this was removed by filtration, the filtrate evaporated to dryness, and extracted with ether. The ethereal solution on evaporation deposited orange-red crusts of hydroplatinocyanic acid. We may here mention that the precipitation of the barium salt with sulphuric acid is a very troublesome process, even when the solutions are hot and dilute, as it is not easy to see the point at which complete precipitation of the barium sulphate occurs, and the least excess of sulphuric acid causes serious decomposition of the hydroplatinocyanic acid as soon as the solution begins to be concentrated, while if any portion of the barium salt is undecomposed, it represents so much material lost.

We found as the result of several experiments, that the most economical method is to weigh both the salt and the sulphuric acid of known strength in the requisite calculated quantities.

Two weighed quantities of the acid thus prepared were taken; to one thallious carbonate was added to produce the reaction $Tl_2CO_3 + H_2PtCy_4 = Tl_2PtCy_4 + CO_2 + OH_2$, the solution being boiled, and allowed to crystallise; the result was a colourless, neutral salt. To the other portion twice the relative amount of Tl_2CO_3 was added; the solution also boiled, deposited on cooling the dark-red salt described in the former paper.

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* *Jour. für pract. Chem.*, vol. cii, p. 144; *Jahresb.*, 1867, p. 281; *Watts's Dict.*, Supp. ii, p. 536.

In order to set the matter definitely at rest, we determined to make an experiment in which no carbonate of thallium was employed, and accordingly barium platinocyanide was decomposed by the addition of thallious sulphate, the precipitated barium sulphate removed by filtration, and the filtrate allowed to crystallise. The resulting heavy crystals were perfectly colourless, and had the same silky lustre and general appearance as those obtained by treating $Tl_2PtCO_3PtCy_4Tl_2$ with warm nitric acid, or by exactly neutralising H_2PtCy_4 with Tl_2CO_3.

In the former paper one of us called attention to the great value of Frankland and Armstrong's combustion method for water analysis as a means of ultimate organic analysis in general. We therefore, as in the former case, made our analyses by that method; 0·1349 grm. of the salt gave 0·00891 C., and 0·01047 N., and in a platinum determination 0·6215 grm. gave 0·1746 Pt. These results (*a*) are in complete accordance with those formerly obtained by one of us in the analysis of the platinocyanide left on treatment of the red salt with an acid (*b*), which we again quote for comparison:—

	Theory.	Per cent.	Found.	
			a.	*b*.
Tl_2	408	57·51		
Pt	197·4	27·82	28·09	—
C_4	48	6·76	6·60	6·78
N_4	56	7·89	7·76	7·91
	709·4	99·98		

These numbers, we think, show conclusively that the salt described by Carstanjen was really the double carbonate, and that thallious platinocyanide is a colourless compound.

We have to thank our friend, Mr. T. Farries, for kindly placing at our disposal a large portion of the thallious carbonate used in these experiments.

XVIII.—*Note on Persulphocyanic Acid.*

By R. W. Atkinson, B.Sc. Lond., Professor of Practical Chemistry
in the University of Tokio, Japan.

The constitution of this body still remains a matter of uncertainty; for of the several possible formulæ, experiments hitherto undertaken do not pronounce in favour of the one rather than of the other. Two different formulæ have been proposed, either of which would explain the reactions of the acid so far as they are at present known, but one of which would seem to be a closer expression of certain properties to be described.

The following decompositions must be indicated by any proposed formulæ:—

1st. Hydric iodide in the nascent state yields carbonic disulphide, and hydriodide of sulphurea.

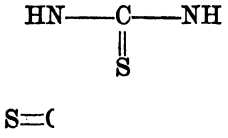
$$C_2H_2N_2S_3 + 2H + HI = (CS)N_2H_4.HI + CS_2.$$

2nd. Nascent hydrogen (tin and hydric chloride) forms hydrochloride of sulphurea.

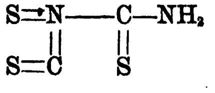
3rd. Persulphocyanic acid combines with one molecule of aniline, with separation of one atom of sulphur:—

$$C_2H_2N_2S_3 + C_6H_7N = C_2H_2N_2S_2.C_6H_7N + S.$$

There is thus a very close connection between persulphocyanic acid and sulphurea, and this connection is best explained in the formula proposed by L. Glutz (*Deut. Chem. Ges Ber.*, iii, 343), in which we see that by the addition of two atoms of hydrogen, sulphurea and carbonic disulphide would be formed. The formula proposed by A. Henninger (*Wurtz's Dictionnaire de Chimie*), also explains this reaction, though not quite so easily.



$$\begin{array}{cccccc} & \mathrm{HN} & - & \mathrm{C} & - & \mathrm{NH} \\ & & & \| & & \\ & & & \mathrm{S} & & \\ \mathrm{S{=}(} & & & & & \end{array}$$



$$\begin{array}{ccccc} \mathrm{S}{=} & \mathrm{N} & - & \mathrm{C} & -\mathrm{NH_2} \\ & \| & & \| & \\ \mathrm{S}{=} & \mathrm{C} & & \mathrm{S} & \end{array}$$

In order to throw some further light upon the properties of this body, the following experiments were carried out, and, though they are not complete, it may be of some interest to publish them as they are.

The substance employed was prepared in the usual way by passing a current of hydric chloride through a saturated solution of potassic sulphocyanate. A thick magma of yellow crystals was formed, which was thoroughly washed with cold water, after which it was dissolved in boiling water and crystallised. This is a somewhat tedious operation when a considerable quantity is required, because the amount dissolved by boiling water is so small that a large number of boilings and filtrations has to be made. The nature of the decomposition by which the persulphocyanic acid is prepared has not hitherto been explained, but the author hopes at a future time to return to this question. It is, however, to be noticed that the composition of the precipitate which has merely been washed with cold water differs from that of the product obtained by crystallisation from hot water. It follows, therefore, that the process given in most books for preparing the acid by merely washing with cold water is not sufficient to yield a pure product.

The acid crystallises from hot water in long and often curved, woolly tufts, presenting a remarkable appearance. After drying in the air and pressing between blotting-paper, these crystals do not lose more than a trace of moisture when heated to 120° in an air bath. When they are placed in contact with cold water and a piece of blue litmus paper, no change of colour is produced at ordinary temperatures; but when the liquid is warmed, the paper becomes faintly reddened, the colour increasing in intensity as the boiling is prolonged. If this liquid be now tested by the addition of barium chloride solution, it is easy to prove the presence of sulphuric acid. This decomposition, although slight, is sufficient to prevent any deductions being drawn as to the effect of persulphocyanic acid upon litmus paper.

Persulphocyanic acid dissolves to a slight extent in cold alcohol, the solution assuming a distinct yellow colour, and it dissolves in boiling alcohol to a much greater extent. One litre of alcohol containing 89 per cent. dissolves at 12·5° 1·58 gram of acid, and at the boiling point dissolves 12·774 grams.

When silver nitrate is added to a warm aqueous solution of the acid, a light yellow precipitate is first produced, which almost immediately becomes orange-yellow, and afterwards passes through various shades of orange to black. If a cold alcoholic solution of the acid be employed, the precipitate remains undecomposed for a much longer time, especially if the temperature be kept low, but even at ordinary temperatures (from 15° to 20° during the time these experiments have been conducted) after two or three hours, the decomposition is very pronounced. The author, however, noticed that on one or two days when the temperature was as low as 10° or 12°, the decomposition was not nearly so rapid as under ordinary circumstances. Ammonia added to the yellow silver precipitate dissolves it, producing a dark-brown solution, which is reprecipitated by the addition of hydric nitrate.

Mercurous nitrate produces a light-yellow precipitate, which is insoluble in cold nitric acid, but on heating dissolves with effervescence, leaving a white precipitate, soluble in aqua regia, and not blackened by ammonia.

Solution of iodine, when heated with the acid, becomes decolorised, producing at the same time an orange-red precipitate. This is soluble to some extent in water, and yellow crystals are deposited, which are alluded to by A. Fleischer (*Deut. Chem. Ges. Ber.*, iv, 190), but the author has been unable to prove the presence of iodine in these crystals. They possess, indeed, the appearance of ordinary persulphocyanic acid, and perhaps are produced by the decomposition of the iodine precipitate.

The production of compounds with silver and with mercurous mercury leads to the question of the composition of these bodies. There appear to be possible only two compounds in each case, there being but two atoms of hydrogen in the acid. The composition of the silver salt has only been approximately determined, as it undergoes decomposition so quickly; but if there can be produced two silver compounds only, it would appear that the yellow precipitate has the formula $Ag_2C_2N_2S_3$.

The following experiments were made to ascertain the weight of the silver compound relatively to the acid employed:—

(1.) 0·2857 grm. acid was dissolved in alcohol (sp. gr. = 0·8254 at 12·5°) with the aid of heat; the solution then allowed to cool, and an excess of an alcoholic solution of silver nitrate added. The precipitate was quickly collected upon a weighed filter-paper, washed with cold alcohol, dried in the air at first, and afterwards at 100°, until the weight was constant. The precipitate thus obtained weighed 0·6705 grm. If the composition of the silver compound were $Ag_2C_2N_2S_3$, the weight of the precipitate should be 0·6933 grm.

(2.) 0·0235 grm. acid was dissolved in alcohol as in (1), and precipitated by an alcoholic solution of silver nitrate, containing a weight of metallic silver corresponding to four atoms, thus $H_2C_2N_2S_3 : Ag_4$; the compound was collected as above. It weighed 0·0580, the hypothetical weight for $Ag_2C_2N_2S_3$ being 0·05703.

(3.) 0·0573 grm. acid treated as in (2), with four atoms of silver in alcoholic solution, yielded a precipitate which weighed 0·140 gram. Theory = 0·139 gram.

(4.) 0·0345 grm. acid treated as above with two atoms (the weight theoretically necessary), yielded a precipitate which weighed 0·0745 grm. Theory = 0·0837.

From the last experiment it seems that in order to precipitate the whole of the acid, it is necessary to add more than the theoretically exact amount of silver. The following experiments show the amount of silver which enters into the composition of the precipitate.

(5.) The precipitate obtained in (2) was ignited, and the resulting metallic silver dissolved in nitric acid and estimated as chloride. It contained 0·032 grm. silver. Theory for $Ag_2C_2N_2S_3$ = 0·0338.

(6.) The precipitate obtained in (3) contained 0·0839 grm. silver. Theory = 0·0825.

(7.) 0·0965 grm. acid was dissolved in alcohol; three atoms of silver in alcoholic solution added, the precipitate quickly collected, washed, dried, and ignited. The residue was dissolved in nitric acid, and the silver estimated as chloride. The silver amounted to 0·1549 gram. Theory = 0·139 gram Ag.

(8.) 0·093 grm. acid treated as in (7) with three atoms of silver yielded a precipitate which contained 0·1356 gram Ag. Theory = 0·1381 gram Ag.

(9.) 0·1695 grm. acid treated with a little more than the equivalent quantity of silver nitrate yielded a precipitate containing 0·2446 gram Ag. Theory = 0·2441 gram Ag.

(10.) The precipitate obtained in (4) by the use of an equivalent quantity of silver nitrate contained 0·0391 grm. Ag. Theory = 0·0501. The weight of silver entering into the composition of the precipitate is thus less than it should have been if the whole of the acid had been thrown down, a result confirming Exp. (No. 4).

These results therefore lead to the conclusion that a weight of silver approaching two atoms enters into the reaction between the two substances. They distinguish between the formulæ $Ag_2C_2N_2S_3$ and $AgHC_2N_2S_3$. Whether such a compound as the latter exists remains to be proved. It would be of peculiar interest as an acid silver salt. On one occasion, after boiling the silver salt with nitric acid, a yellow or orange-yellow substance was left undissolved, and long boiling failed to decompose it. The precipitate was collected, washed with hot water, and a portion of it ignited in a porcelain crucible, a residue of silver and carbon being left and sulphurous acid being evolved. The silver was determined in the usual way and amounted to 43·18 per cent. The acid silver salt, $AgHC_2N_2S_3$, would contain 42·02 per cent. Ag. Other attempts to procure this substance in a similar manner have failed, but the author still hopes for success in another direction.

When the yellow silver persulphocyanate is boiled with water, it quickly decomposes with effervescence and with production of a heavy black precipitate, which rapidly sinks to the bottom of the liquid. Attempts were made to ascertain the nature of the decomposition by collecting this black precipitate and determining its composition, but the results obtained vary so widely from one another in different experiments, apparently depending upon the proportion of silver nitrate present and upon the temperature, that no single equation will represent the decomposition under all circumstances.

(11.) 0·04 grm. acid was dissolved in hot water and boiled with a considerable excess of aqueous silver nitrate till no further action was observable. The black precipitate was collected, dried at 100 C., and weighed. The weight was 1·739 gram. It was then dissolved in fuming nitric acid and the silver estimated as chloride. The silver amounted to 1·463 gram. Taking the molecular weight of persulphocyanic acid as 150 ($H_2C_2N_2S_3 = 150$), the weight of the black precipitate would correspond to 652·1 per molecule of acid, and the silver to 548·6 per molecule.

(12.) A second experiment carried out in the same way with a similar excess of silver nitrate gave the numbers 658 per molecule of acid for the black precipitate and 560 for the silver contained in the precipitate.

(13.) 0·1456 gram of acid boiled with water and a moderate excess of silver nitrate yielded a black precipitate which contained 0·490 gram Ag. This corresponds to 505 per molecule of acid.

(14.) 0·0795 gram of acid treated as in (13) with a moderate excess of silver nitrate yielded 0·316 gram of black precipitate containing 0·2712 gram Ag. These numbers correspond to 607·5 of black precipitate and 512 of silver per molecule of acid.

(15.) 0·0277 gram of acid, treated as above with a slight excess of silver nitrate, gave 0·106 gram of black precipitate and 0·087 grm. Ag. These numbers correspond respectively to 574 and 471 per molecule of acid.

A consideration of these results will show that the weight of black precipitate and of silver is greater where the nitrate of silver solution is used in excess. It will also be noticed that the percentage of silver in the black precipitate is greater when a considerable excess of nitrate of silver was used than when only a slight excess was employed. Thus the percentages of silver in the previous experiments are—

Experiment	11.	12.	14.	15.
Percentage of silver	84·1	85·3	84·2	82·1

(16.) Some quantity of the black precipitate was prepared by boiling the acid with a small excess of silver nitrate. After washing and drying at 100° C. a weighed portion was heated with fuming nitric acid, when it was attacked with strong effervescence commencing even in the cold, and becoming violent on gently heating. When the substance was completely dissolved, the silver was estimated as chloride and the sulphur determined in the filtrate as baric sulphate—

	(1.)	(2.)
Silver..............	81·12	81·10
Sulphur............	17·45	16·85
Diff. from 100	1·43	2·05
	100·00	100·00

The ratio of the atoms of silver to the atoms of sulphur is 3 : 2.

(17.) In experiments (11) and (12) the silver and sulphur were determined—

	(1.)	(2.)
Silver................	84·1	85·3
Sulphur..............	14·7	14·3
Diff. from 100	1·2	·4
	100·0	100·0

The ratio of silver atoms to sulphur atoms is in (1) 17 : 10, and in (2) 17·5 : 10.

The only known compound of silver and sulphur is the sulphide Ag_2S in which the ratio of the atoms is 2 : 1; it is probable therefore that the black precipitate is a mixture of sulphide of silver and some substance containing a larger proportion of sulphur, perhaps silver sulphocyanate, while the ratios in which the two products are formed changes with differences in the amount of silver nitrate employed. With an excess of silver nitrate the proportion of silver sulphide in the black precipitate will be greater, as is seen from experiments (16) and (17). In the former, where only a slight excess of nitrate of silver was used, the ratios are 15 : 10, while in the latter, where a considerable excess was used, the ratios are 17 : 10 and 17·5 : 10.

The following equation is given, not as being an exact representation of any particular experiment, but as probably indicating the general nature of the reaction—

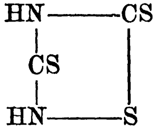
$$Ag_2C_2N_2S_3 + 3AgNO_3 = 2Ag_2S + AgCNS + CO_2 + N_2O_4 + N_2O_3.$$

The author hopes to be able to communicate further experiments upon this subject on a future occasion.

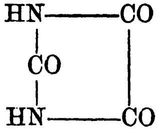
The yellow precipitate produced by mercurous nitrate in a solution of persulphocyanic acid does not appear to be decomposed by boiling like the silver salt. Only a single experiment was made upon this body.

(18.) 0·147 gram of the acid gave 0·553 grm. of the precipitate dried at 100° C. If it has the formula $Hg'_2C_2N_2S_3$ the weight of the precipitate would be 0·537. The precipitate was dissolved in aqua regia and the mercury determined as sulphide. The weight of mercury obtained was 0·3925. The formula $Hg'_2C_2N_2S_3$ would require 0·392 gram. It seems therefore that the yellow precipitate is represented truly by the formula given.

If we adopt the formula given by L. Glutz (*loc. cit.*) for this acid, the existence of the salts above described can be accounted for as easily as the silver salt of parabanic acid. There is, indeed, some resemblance between the two bodies which would justify somewhat similar formulæ. Thus parabanic acid forms a silver salt containing two atoms of silver, and it decomposes into urea and hydric oxalate by treating with acids. The resemblance will be better seen by a comparison of the explicit formulæ.



Persulphocyanic acid.
(L. Glutz.)



Parabanic acid.

The silver salts of each acid are formed by replacement of hydrogen in the same way, the metal becoming united with nitrogen, while the greater stability of the parabanate is explained by the smaller attraction of silver for oxygen than for sulphur.

XIX.—*On Di-isopentyl or Diamyl.*

By Harry Grimshaw, F.C.S., late Demonstrator in the Laboratory of the Owens College.

Diamyl was first prepared by Wurtz, who obtained it by the action of sodium upon amyl-iodide (*Ann. Chim. Phys.*, 3rd Series, xliv, 281, 1855). Its boiling point he found to be 158°, and its specific gravity 0·7413 at 0°, and 0·7282 at 20°. Later, Schorlemmer prepared it, and found it to boil between 158° and 159°, with a specific gravity of 0·7275° at 14° (*Proc. Roy. Soc.*, xiv, 172), and obtained from it, by the action of chlorine, a mono-chloride, which he converted into the corresponding acetate and alcohol. He afterwards showed that chlorine converts the normal paraffins into a mixture of a primary and secondary chloride (*Phil. Trans.*, 1872, i, 111). That this also occurs with hydrocarbons belonging to the "iso" group was shown in the case of ethylamyl, referred to below. As diamyl belongs to the "di-iso" group, it appeared of importance to ascertain whether the same action also took place with this hydrocarbon, and I therefore commenced a new research upon it.

The diamyl used was prepared from amyl bromide, boiling from 119° to 123°. The bromide was decomposed by means of sodium in the manner described in my paper on ethyl-amyl (*Chem. Soc. J.*, [2], xi, 309), by means of a flask placed in an oil-bath, and connected with a well-cooled, inverted condenser.

The following were the quantities taken in each operation. Of the bromide, 300 grams, and of sodium, 50 grams. These were heated up to a temperature of 100°, the sodium being added gradually. No action took place in the cold, as was also noticed by Wurtz, but it commenced at about 100°, and at this point it was noticed that a small portion of a very volatile liquid was formed and distilled over, through the inverted condenser; but this was not further examined. When the action of the sodium on the bromide was becoming slow, the temperature was raised to 140° or 150°, and kept at this for about 6 hours, and the liquid then distilled off.

The diamyl thus obtained was allowed to stand over sodium for a week, rectified over sodium, and distilled. It was then placed in contact with strong sulphuric acid for a day, and after removal of the acid, treated with more sulphuric acid and nitric acid. The diamyl was then dried with caustic potash and sodium, and subjected to fractional distillation, and the portion coming over from 157° to 159°, taken for the further operations. The following is the analysis:—

0·258 grm. diamyl gave 0·801 grm. CO_2, and 0·361 grm. H_2O.

	Percentage.	
	Calculated.	Found.
C_{10}	84·51	84·67
H_{22}	15·49	15·54

On repeated purification and fractionating, pure diamyl was found to boil at 160° under a barometrical pressure of 751 mm.

Chlorination of the Diamyl.

Dry chlorine gas was passed into the vapour of the boiling hydrocarbon, just as in the case of the ethyl-amyl, and by means of an arrangement similar to the one described in my paper above mentioned. In the presence of too much light, or of excess of chlorine, ultimate decomposition and ignition of the vapour of the hydrocarbon took place much more readily than with the vapour of ethyl-amyl.

On fractionating the chloride thus obtained, the whole of it came over from 198° to 217°; and principally in two portions boiling respectively, from 198° to 202°, and 208° to 213°. A little above 220°, the chloride began to decompose. The action of the chlorine always darkened the liquid, even when no ignition of the gas in the vapour of the hydrocarbon was observed.

Formation of the Acetates.

The decomposition of the chloride was effected as usual, by heating in closed tubes with acetic acid and an acetate. In order to obtain the best possible yield of the acetate from the chloride, experiments were made to compare the amounts obtained by the use of potassium, sodium, and lead acetates respectively. In various trials, 12 grams of the diamyl chloride and the same volume of acetic acid were heated with 12 grams of lead acetate, or 6 grams of sodium acetate, or 9 grams of potassium acetate. The last was found to yield the greatest relative amount of the olefine, and also with it, the highest temperature was needed for decomposition. The proportion of olefine yielded by the sodium and lead acetates was considerably smaller, and the decomposition took place more easily. The lead salt was finally selected on these accounts, and as with it, the action was accomplished at the lowest temperature. The decomposition was found to be complete when the tubes had been kept at 160° to 170°, for about 48 hours. The lead acetate, before use, was rendered anhydrous.

The liquid resulting from this operation was washed with water and dried with anhydrous potassium carbonate, and on fractionating, began to distil at 180°; nearly one-third coming over below 190°, and the temperature reaching 240°, above which there was very little residue, which began to decompose and give off a strong odour of acetic acid. On fractionating, nearly all came over between 198° and 215°, as a colourless, mobile, light liquid having a fruity smell.

Formation of the Alcohols.

The liquid above obtained was mixed with an excess of caustic potash and a little water, so as to make a partially solid mass, which was allowed to stand for 24 hours. The flask containing the mixture was then placed in connection with an inverted condenser and boiled for 6 hours. The liquid thus obtained was separated, dried over caustic potash, and then over potassium carbonate, and subjected to fractional distillation. On the first fractionation, the liquid began to boil at 202°, and the temperature reached 224°. On the third fractionation, boiling commenced at 196°, and of the first portions coming over, the greater part was between 202° and 203°; whilst a smaller portion distilled from 207°—214°, principally between 211° and 213°. Both the light, colourless liquids, thus separated, had an odour resembling that of oranges, slightly differing in the two cases, the higher-boiling liquid being the more powerful. The amount of this latter was only about one-third of that of the lower-boiling portion.

Oxidation of the Alcohols.

The separation of the above two portions, by fractionation, being but very imperfect, they were mixed together and subjected to the action of an oxidising mixture of 2 parts bichromate of potash, 3 parts sulphuric acid, and 8 parts water, a weaker mixture, with 10 parts water, being found not to act at all readily. The action was allowed to go on in the cold for 48 hours, with frequent shaking, and at the end of that time, there was a slight excess of the chromic acid solution, as was shown by the colour of the mixture. The whole was then distilled and the light oily liquid separated from the distillate. The residue was distilled again with water, and all the aqueous distillates neutralized with carbonate of soda, and evaporated down nearly to dryness. The sodium salt thus formed was decomposed by diluted sulphuric acid and distilled. The acid distillate thus obtained was converted into the silver salt by boiling with carbonate of silver, and analysed. The following are the numbers:—

0·084 gram of the salt gave 0·054 grm. Ag.

	Percentage of Ag.	
	Calculated.	Found.
$C_2H_3O_2Ag$	64·67	64·29

The light liquid before mentioned, which was separated from the cold oxidation-product, was dried over potassium carbonate for some days and fractionated. It began to boil at 203°, and the temperature reached 218°. Finally, almost the whole came over between 208° and 212°, especially about 209°. A portion of this liquid was submitted to the action of sodium bisulphite, but no crystalline compound could be obtained.

Oxidation.

The bichromate mixture acted but slowly on this liquid, even when heated with it. CO_2 was continually given off. After boiling for 24 hours under an inverted condenser, the acid solution was distilled off, a sodium salt formed and decomposed as before, and also the silver salt formed, during which latter operation a strong smell of valerianic acid was given off. The analysis of the silver salt was as follows:—

0·227 Ag salt gave 0·1445 Ag = 63·66 per cent. Ag.
$C_2H_4O_2$ contains 64·67 „ „
$C_6H_{10}O_2$ „ 51·67 „ „

A larger quantity of the liquid was oxidized and the sodium salt prepared. This was partially decomposed by a few drops of dilute sulphuric acid, and the acid liquid distilled off and boiled with Ag_2CO_3, this being repeated three times.

1st fraction 0·0105 Ag salt gave 0·0053 Ag = 50·47 per cent. Ag.
2nd „ 0·0516 „ „ „ 0·0394 = 63·47 „ „
3rd „ 0·0489 „ „ „ 0·0321 = 64·66 „ „

The above being the whole of the results which time has allowed me to obtain up to the present, the research remains very incomplete; but, failing my being able to work the subject thoroughly out in a short time, I am happy to be able to state that it will be taken up in the laboratory of the Owens College.

XX.—*On the Oxidation-products of the Aloïns.*

By William A. Tilden, D.Sc. (Lond.).

[Note.—Barbaloïn is obtained from Barbadoes aloes; socaloïn from Socotrine, or Zanzibar aloes; nataloïn from Natal aloes. For preparation, properties, composition, and derivatives of these substances, see Stenhouse (*Phil. Mag.* [3], xxxvii, 481); Flückiger (*Year-book of Pharmacy*, 1871); Tilden (*J. Chem. Soc.* xxv, 204; *Pharm. J. Trans.* [3], ii, 441, 845; vi, 208: *Chem. News*, May, 1872); Schmidt (*Deut. Chem. Ges. Ber.*, viii, 1275; *Archiv. der Pharmacie*, 1876.]

When nataloïn is digested with a 10 per cent. solution of bichromate of potassium acidified with the proper quantity of sulphuric acid, it yields a large quantity of carbonic acid, and the liquid retains abundance of acetic acid. Nothing else could be obtained from the solution, either by evaporating or by extracting with ether.

When, however, a solution of barbaloïn or socaloïn is mixed with the chromic liquor, it becomes blood-red, and on heating effervesces freely, from escape of carbonic acid, depositing a brown precipitate. The liquid filtered from the precipitate contains very small quantities of acetic acid.

In order to examine the precipitate, it was filtered off, digested for a short time with a weak bichromate solution, then collected, washed with water, dried, and dissolved in boiling rectified spirit. The solution on cooling deposited yellow granules, which were not perceptibly crystalline under the microscope. The result of the analysis of the substance prepared from barbaloïn was as follows:—After drying at 100°, it left 1 per cent. of ash consisting of chromium oxide. Allowing for this, the numbers obtained by combustion were:—

	I.
C	64·3 per cent.
H	3·5 „

After being several times re-deposited from alcohol, it was again analysed, having been dried at 130°. The following are the results in per cents.:—

	II.	III.
C	64·2	64·2
H	3·1	3·1

As the substance still contained traces of chromium, it was dissolved in glacial acetic acid and precipitated by adding water, which threw it down as a yellow precipitate. This process, however, failed to remove the last traces of chromic oxide, which seems to adhere to it with great obstinacy. It was dried for analysis at 130°, and then gave the following results:—

	IV.
C	63·3
H	3·2

A portion of the substance prepared by the same process from Zanzibar aloes, and purified by repeated solution in and deposition from acetic ether was next examined. It was boiled with a large volume of water, and the golden-yellow solution filtered from the residue, and acidified with sulphuric acid. An orange-yellow flocculent precipitate was thus obtained, which was collected, washed, dried, and dissolved in acetic ether. The solution concentrated deposited orange granules and crusts, which under the microscope appeared doubtfully crystalline. It gave on combustion—

	V.
C	63·8
H	3·4

An attempt was made to purify the substance by sublimation, but the greater part was charred, and the sacrifice of material was too great to warrant a repetition of the experiment. 6 grams were very cautiously heated in a long piece of combustion-tubing, through which a somewhat rapid current of carbonic anhydride was kept passing. A yellow pulverulent sublimate, containing a few orange needles, was obtained, which, when collected, weighed altogether 3 decigrams. This was dissolved in acetic ether and crystallised out, partly in orange granules, partly in paler-coloured needles.

·2290 gram gave ·5178 CO_2, and ·0712 OH_2, corresponding with—

	VI.
C	61·6 per cent.
H	3·4 „

The properties of the oxidation-product of barbaloïn agree in every respect with those of the compound obtained from socaloïn, and I regard them as identical. For convenience sake I propose to call this compound *aloxanthin*. In the greatest state of purity in which I have been able to obtain it, it forms an orange granular powder, which melts imperfectly at 260°—265°, subliming slowly at about the same temperature in orange scales and dust. It is but slightly soluble in water, and is reprecipitated almost entirely on addition of an acid. It is scarcely soluble in bisulphide of carbon, or in chloroform. Alcohol dissolves it sparingly, also ether, but its best solvents are ethyl acetate and glacial acetic acid. Aloxanthin dissolves in solution of caustic soda, forming a bright cherry-red solution, which shows no bands before the spectroscope, but a continuous absorption, starting from the violet, and extending to about the middle of the yellow. There is no difference in this respect between the sublimed and the unsublimed substance.

When aloxanthin is heated with zinc dust, it yields a considerable quantity of a hydrocarbon having a greenish fluorescence.

Three specimens were obtained, having practically the same melting point:—

1. From oxidation-product of barbaloïn, melting point, 205°.
2. „ „ socaloïn, „ 203°.
3. „ „ barbaloïn, „ 204°.

This hydrocarbon oxidised by glacial acetic acid and chromic trioxide gave a product which, when purified by solution in ammonia and sublimation, melted at 283° (melting point of anthraquinone-carbonic acid, 280°). There can be no doubt, therefore, that the hydrocarbon obtained by reduction of aloxanthin consists principally of methylanthracene, and not of anthracene. This agrees with the observation of

Schmidt (*Deut. Chem. Ges Ber.*, viii, 1275), that the aloïn of socotrine aloes yields methyl-anthracene.

Aloxanthin has no affinity for mordants. When fused very gently with caustic potash, it forms an indigo-blue mass, which, dissolved in water, forms a purplish solution. From this acids throw down a yellow precipitate, which, however, is also incapable of combining with iron or alumina, or nearly so. Aloxanthin forms insoluble compounds, with baryta and with lead.

The results of all the analyses of aloxanthin already detailed give a mean of

63·5 per cent. of carbon,
3·3 per cent. of hydrogen.

These results, coupled with the fact that it yields methyl-anthracene by reduction, point to the formula,

$$C_{15}H_{10}O_6,$$

which would represent aloxanthin as a methyl-tetroxyanthraquinone,

$$C_{14}H_3(CH_3)(OH)_4O_2.$$

A body of this composition contains—

C .... 62·9
H .... 3·4

The last three analyses, in which the purest material was employed, although not closely concordant among themselves, give a mean which is very near to these numbers, viz.:—

C .... 62·9
H .... 3·3

Confirmation of this formula is derived from the analysis of the acetyl-compound, which was prepared by boiling aloxanthin with acetic anhydride. After deposition from glacial acetic acid, and then from alcohol, this compound appeared in the form of brownish granules, very like the original substance. It was analysed by boiling with alcoholic soda, then adding water, evaporating the alcohol, and precipitating with hydrochloric acid. The small quantity of substance contained in the washings was recovered by shaking up with ether, and collecting the ethereal solution. ·485 grm. of acetyl-compound gave ·422 grm. of aloxanthin, dried at 100°. According to the formula, $C_{15}H_9(C_2H_3O)O_6$, this quantity should have yielded ·4229 grm. of aloxanthin. The compound is, therefore, a mono-acetyl derivative. I have not prepared any other.

When aloxanthin is treated with fuming nitric acid in the cold, no gas is evolved, but the yellow solution, when mixed with water, gives a precipitate consisting of a yellow nitro-acid, which is not quite insoluble in acidulated water, and dissolves in alkalis and in potassium acetate, forming a deep red solution. Its potassium salt is very soluble in water, less so in presence of excess of potassic acetate. The alkaline solution warmed with ammonium sulphide, becomes deep blue, like a solution of hydrochrysamide. Chrysammic acid is, however, not formed, but is produced, together with what seems to be picric acid, only by the prolonged action of hot nitric acid upon aloxanthin. All these characters belong to the uncrystallisable acid, known as aloetic acid, which accompanies chrysammic acid as a product of the action of nitric acid upon Barbadoes or Socotrine aloïn.

Representing aloetic acid as trinitroaloxanthin, it will be seen that the analytical results obtained long ago by Schunck and Mulder, come very near to the requirements of the hypothesis, the discrepancies doubtless arising from the extreme difficulty of completely separating aloetic acid from chrysammic acid. The presence of the latter substance would lower the carbon, and raise the percentage of nitrogen.

		Aloetic acid.		
	Trinitroaloxanthin, $C_{15}H_7(NO_2)_3O_6$. Calculated.	Schunck.	Mulder. (Mean.)	Chrysammic acid. $C_{14}H_4(NO_2)_4O_4$. Calculated.
C	42·7	40·7	41·5	40·0
H	1·6	1·7	1·5	·9
N	9·9	11·6	14·4	13·3

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Spectroscopical Notes. By H. W. VOGEL (*Deut. Chem. Ges. Ber.*, x, 373—375).—A cut oriental garnet of ruby-red colour gave an absorption-spectrum containing a band α, between F and *b*, a weaker one, γ, from *b* to E, and darker one, β, near D. A brownish Bohemian garnet gave a similar spectrum, only α and γ became one, while a pyrope showed β only in sunlight, and the green, blue, and violet were completely absorbed.

Ruby shows an indistinct band between E and D, while ruby-glass coloured by gold-purple gives a similar one, which is however more distinct and nearer to E.

The purpurin reaction for magnesia cannot be seen if much lime be present, as it gives alone an indistinct band-spectrum. But if no lime be present, the alkaline purpurin bands make their appearance and might be mistaken for magnesia. These bands are removed by adding sal-ammoniac; on adding to 2 c.c. of pure water, 3 drops of tincture of purpurin and one drop of dilute ammonia, the bands are very intense, but 5 drops of a solution of ammonium chloride (1 : 10) make the bands disappear almost completely, a pale shadow in the green remaining. If now 1 drop of magnesium chloride (1 : 1000) be added, its characteristic spectrum appears at once.

When too much lime is present, it is best removed with ammonium chloride and ammonium carbonate; the liquid is allowed to settle and drawn off, and the last trace of lime precipitated by ammonium oxalate.

To detect alumina in presence of iron, the latter is converted into a ferric salt, potassium thiocyanate is then added, and the liquid shaken with ether until the aqueous solution is pale yellow, which on addition of purpurin shows the alumina-spectrum. The reaction becomes much less delicate in presence of much manganese. C. S.

Electro-metallurgy and Electro-Chemical Actions. By A. THENARD (*Compt. rend.*, lxxxiv, 706—708).—The current of a magneto-electric machine employed in producing deposits of copper, was made to pass through baths containing plates of copper as electrodes, and charged with solution of copper to which some sulphuric acid was added. It was found that the total quantity of copper deposited in the circuit increased with the number of the baths, which were arranged in a series like the cells of a battery. The quantity of copper deposited on each anode decreased with the increase of their number, but the quality of the deposit was better when a larger number of baths were employed. R. R.

Electrosilicic Light. By G. PLANTÉ (*Compt. rend.*, lxxxiv, 914—916).—When a platinum wire crosses a capillary tube filled with a saline solution, and a current of electricity caused by 60 to 250 to 300 secondary couples (depending on the nature of the salt) is passed through the wire, the glass fuses, even in contact with the liquid, and emits a dazzling light. When the knob of platinum has become coated with glass, it is isolated from the liquid, and the light disappears. With a solution of salt, 250 to 300 secondary pairs are necessary: with nitre, 60 pairs equal to 90 Bunsen's cells. The intensity of this light depends on the nature of the silicate (glass), which is devitrified by the heat, while a white vapour with slight alkaline reaction is evolved. The spectrum of the light is not that of the lime combined with the silica; a fragment of calc-spar, under the same circumstances gave a calcium spectrum. The rays of silicon are so weak as not to be visible through the very bright continuous spectrum, in the same way as the spectrum of carbon is not visible in the incandescent voltaic arc.

But that silicon is the cause of the light is shown by its formation with crystals of pure silica, and it probably arises from the incandescence of *silicon* liberated from the silica by the intense heat.

W. R.

Manufacture of Carbon Points for the Electric Light. By F. CARRÉ (*Compt. rend.*, lxxxiv, 346—348).—Attempts were made to impregnate the carbon terminals with various salts, in order to modify the light. The following results were obtained:—

1. Potash and soda double the length of the electric arc, and render it silent; they combine with the silica contained in the carbon, and the silicate is deposited in the form of vitreous globules at 6 or 7 mm. from the points. These substances increase the light in the ratio 1·25 : 1.
2. Lime, magnesia, and strontia increase the light in the ratio 1·3—1·5 : 1, with production of various colours.
3. Iron and antimony cause an augmentation of light in the ratio 1·6—1·7 : 1.
4. Boric acid increases the hardness of the carbon points, but does not increase the light.

The manufacture of carbon points by impregnating pure and homogeneous charcoal with solutions of the above substances is convenient and economical, but it is better to mix the substances with the charcoal in powder.

In the latter case the carbon is purified by washing, &c.; it is then mixed with the salt, moistened with a solution of gum, and pressed through a wire-drawing machine by means of a powerful hydraulic press.

The carbon terminals thus made are very superior to those obtained from gas carbon; they are very tenacious and rigid, and being perfectly homogeneous, the light obtained by their means is much less liable to variation; further, they do not explode when ignited, as there is no enclosed gas.

F. D. B.

Account of Researches by Dr. E. Root of Boston, concerning the Permeation of Platinum by Electrolytic Gases. By H. HELMHOLTZ (*Pogg. Ann.*, clix, 416—420).—The results communicated by Professor Helmholtz in 1873 to the Academy of Berlin, led him to the belief that by galvanic polarisation, not only the particles of gas superficially imposed, but also those deeper in the substance of the platinum must play an important part, the probability of which fact has already been brought forward in the researches of Graham on palladium and platinum. To demonstrate exactly the occlusion of the gases by platinum through galvanic polarisation, Helmholtz supplied Dr. Root with the means of investigating whether the hydrogen given off by galvanic polarisation on one side of a platinum plate could be remarked after some time on the other side, so that galvanic polarisation might be brought about. These researches have given the experimenters the results they anticipated. The apparatus used was as follows: To both sides of a platinum plate 0·02 mm. in thickness placed vertically, were fixed by sealing-wax the open ends of two tubulated glass receivers, one opening of each being fastened to the platinum plate already mentioned, the other open ends being turned in an upward direction. The edges of the platinum plate projected beyond the cement joining it to the glass vessels, so as to prevent any liquid contact between the fluids placed in them. The glass vessels were filled with distilled water acidulated with one or two drops of dilute sulphuric acid and two platinum electrodes were fixed vertically in the open and upturned ends. Before conducting the experiments, the authors tested the purity of the platinum, and the apparatus filled with water was allowed to remain for a considerable length of time to be certain of its junctions being air tight. The experiments are mentioned in detail, but as no general conclusions are stated, it is difficult to form an abstract, and it is therefore advisable that reference should be made to the original paper *in extenso* for the results obtained.

J. M. T.

The Thermo-electric Force of Zinc and Solution of Zinc Sulphate. By L. HERMANN (*Pflüger's Archiv. f. Physiologie*, xiv, 485).—Recent measurements by the compensation method of the power of these elements show the electromotive force to be only approximately proportional to the difference in temperature. For a difference of 100° the force was about 0·072 = $\frac{1}{14}$ Daniell.

F. J. L.

On Attraction and Repulsion of Bubbles by Heat, and on the Constant Vibration of Minute Bubbles. By WALTER NOEL HARTLEY (*Proc. Roy. Soc.*, xxvi, 137, 150).—The paper deals with the bubbles in fluid cavities of crystals, and their behaviour when a source of heat is brought near them. A long course of experiments has revealed the following facts:—

1st. That the bubbles in fluid cavities of minerals are sometimes attracted by a source of heat.

2nd. That bubbles are sometimes repelled by the same source of heat.

3rd. That a rise of 5° or 6° C. above the temperature of the specimen suffices to cause attraction.

4th. That a rise of only $\frac{1}{2}$° C. will in certain cases cause repulsion.

5th. That in certain cases the same bubble was repelled under ordinary conditions, but when its temperature was raised to 60° it was attracted, the source of heat being from $\frac{1}{2}$° C. to 5° warmer than the specimen.

6th. That this could occur in cavities containing liquid carbonic acid as well as water, but that it made no difference whether the carbonic acid was raised above the critical point or not. This affords a means of controlling to some extent the conditions of the experiments, since carbonic acid at a temperature just above its critical point has a tension of 109 atmospheres.

The author shows reasons for not being satisfied with Prof. Tait and Swan's explanations of the movement of bubbles in Iceland spar, noticed by Mr. Lang, of Edinburgh. He states that the warmth of the fingers is sufficient to propel even in a vertical direction a plug of water contained in a capillary tube open at both ends, and he refers the attraction of bubbles by heat to the same cause which occasions this movement. In communications addressed to Mr. Hartley, Prof. Stokes states that this *repulsion* of the liquid is due to the diminution by heat of the surface-tension at one end of the plug of liquid in a tube or side of a bubble in a cavity.

When repulsion of a bubble, or *attraction* of the *liquid*, takes place, it is because a slight rise in temperature effects a disengagement of gas from the water on the side of the bubble nearest to the source of heat, which increases the surface-tension at this side; the bubble is therefore propelled in the opposite direction. Considering that these explanations may meet every fact which he has noticed, the author has abandoned his own theory with regard to this movement. Those who have given great attention to the study of fluid cavities in minerals are acquainted with the occurrence in some granites, and other quartzose rocks, of minute vibrating bubbles. Sometimes they have been seen floating on liquid carbonic acid, but under such conditions they are very rarely met with. They vary in size from $\frac{1}{50,000}$ to $\frac{1}{15,000}$ of an inch in diameter, the more minute bubbles having the most rapid motion. They always move over to the warmer side of the cavities in which they are contained, and any appreciable rise of temperature causes them to cling to that side for a considerable time quite motionless. Since all substances are continually gaining and losing heat, it is impossible to imagine a body which, throughout its entire mass, and at the same instant of time, is one of uniform temperature. It is evident, then, that an easily movable particle of very minute size, which can be set in motion by exceedingly slight rises of temperature, may make the transference of heat from one point to another plainly visible: hence these vibratory motions are considered to afford an ocular demonstration of the continual passage of heat through solid substances. W. N. H.

The Formation of Compounds at a Temperature considerably above that of their Decomposition. By TROOST and HAUTEFEUILLE (*Compt. rend.*, lxxxiv, 946—949).—1. Silicon sesquichloride, Si_2Cl_6, decomposes at 350°, and its decomposition is complete at 800°, thus: $2Si_2Cl_6 = 3SiCl_4 + Si$. But at 1200° the reaction is this: $3SiCl_4 + Si = 2Si_2Cl_6$. If the tube in which the sesquichloride is kept at 1400° be suddenly cooled, the sesquichloride condenses as such; if slowly cooled, it has time to decompose, and tetrachloride and silicon are the only products. Ditte has proved that this is also the case with hydric selenide and telluride.—2. If a porcelain tube containing metallic platinum, and provided with a glass tube in its interior, through which a current of cold water passes, be heated to 1400°, the platinum is converted into tetrachloride, $PtCl_4$, which condenses on the cold glass tube. But at a lower temperature, the tetrachloride is decomposed.—3. Ozone is converted into oxygen at 250°. But at 1300—1400°, a silver tube kept cool by water, placed in the interior of a porcelain tube filled with oxygen, was covered with a layer of dioxide; this is the effect of ozone. It is possible, by drawing off the gas from the interior of the porcelain tube, and quickly cooling it, to prove the formation of ozone by the decolorisation of indigo, and other reactions. At a lower temperature, however, no ozone is formed.—4. If silver be vaporised at 1400° in a porcelain tube, through which a tube cooled with water passes, in presence of oxygen, metallic silver, mixed with a very large proportion of protoxide, condenses on the cold tube. But if the porcelain tube be allowed to cool, no protoxide is formed, as it is all decomposed at a temperature below 1400°.

It is therefore not correct to assume that a substance which undergoes dissociation at a low temperature cannot exist at a higher temperature. W. R.

Condition of Salts in Solutions. By D. GERNEZ (*Compt. rend.*, lxxxiv, 771—773).—Experiments with solutions of sodium sulphate and other salts which form several hydrates, led the author to conclude that there is no ground for supposing that different allotropic varieties of such substances exist in solutions which have been subjected to certain temperatures. R. R.

New Method of Recognising Dissociated Vapours. By L. TROOST (*Compt. rend.*, lxxxiv, 708—713).—The method is illustrated by the case of hydrate of chloral, the vapour of which has a density that has hitherto been held to indicate dissociation into chloral and aqueous vapour. If such be its actual condition, the vapour, having a tension F, will behave like a mixture of equal volumes of dry gas and aqueous vapour, each having the tension $\frac{F}{2}$; and when there is introduced into the mixture a hydrated salt, of which the tension of dissociation is known to be f, and less than $\frac{F}{2}$, the total tension of the vapour in the apparatus will remain unchanged, that is $= F$, for the salt will be in presence of a greater proportion of aqueous vapour than it could itself give off at the same temperature. If, on the other hand, the hydrate of chloral exists undecomposed in the vapour, the salt will be dissociated as in dry gas, and the total tension will consequently be increased, and will tend to become F + *f*.

The salt employed by the author with the hydrate of chloral was neutral oxalate of potassium, which has at 78° a dissociation-tension of 53 mm. The elastic force of the vapour of the hydrate of chloral at 78° was 117·5 mm.; but on addition of the oxalate, the tension in the vessel gradually increased, till 164·5° was reached. The hydrated salt had become dissociated in the vapour nearly as in a dry gas. Therefore, contrary to the received opinion, hydrate of chloral can exist in the gaseous state at 78°, and hence its equivalent in volumes corresponds with 4 vols., and not with 2 vols. R. R.

On the Temperature of Steam formed under Normal Conditions. By F. C. G. MÜLLER (*Deut. Chem. Ges. Ber.*, x, 7, 8).—The dropping which takes place from the bulb of a thermometer immersed in the vapour of a boiling saline solution, might lead to the inference that the temperature of steam formed under such circumstances, is below 100°. This, however, is not the case, for the author finds that the thermometer shows exactly the temperature of boiling water, whether the bulb be silvered, or covered with a bad conductor of heat, such as sealing-wax or paraffin. He therefore concludes that the dropping arises from condensation taking place, not on the bulb, but on the stem. When the latter is heated and enveloped in bibulous paper, the dropping stops almost entirely, while the thermometer marks the same temperature as before. Hence the condensation arises from conduction of heat alone.

The fact stated in a previous paper, that a thermometer having its bulb moistened with a saline solution, and exposed to steam action, marks the boiling point of that solution, can be shown far more strikingly if the stem be enveloped as above, as the otherwise rapid ablution of the salt is checked. There is always, however, a slight dropping, as the thermometer absorbs heat, and radiates it to the colder envelope. C. L. F.

Thermic Phenomena of Iodic Acid. By BERTHELOT (*Compt. rend.*, lxxxiv, 734—740).—The author discusses the thermic phenomena attending the formation of potassium iodide by the reaction between iodine and solution of potash. This reaction is, under the conditions of experiment, accompanied by an absorption of heat; but when the influence of the solvent is taken into account, and the phenomena are referred to the substances in the solid state, it is seen that the reaction is in reality exothermic. A comparison of the thermic data in the parallel reactions explains the decreasing order of stability in iodates, chlorates, bromates; and explains also certain differences in the behaviour of other corresponding halogen compounds. R. R.

A Curious Method of Producing Heat. By J. OLIVIER (*Compt. rend.*, lxxxiv, 550).—A square bar of steel, 15 millimeters in diameter, and 70 to 80 centimeters long, was held against a grindstone with two hands, one at the end of the bar, and the other at the middle. The middle of the bar remained quite cold, while the end farthest from the stone became too hot to touch. This appears to show that metals do not always conduct heat uniformly along their surface.

W. R.

Apparatus for Oxidation. By OSCAR LOEW (*J. pr. Chem.* [2], xv, 327—329).—The apparatus, of which drawings are given, consists of a hollow brass cylinder, 35 cm. long, and 12 cm. broad, resting horizontally, through which pass two axles furnished with paddles, placed alternately, so that on the revolution of the axles, these paddles pass one another in opposite directions. In the top of the cylinder, the front of which is movable to allow of cleaning, are openings for the entrance and egress of oxygen, as also one for the introduction of a thermometer.

E. W. P.

Lecture Experiment on Torpedoes. By A. BASAROW (*Deut. Chem. Ges. Ber.*, x, 25).—A small parchment cylinder is filled with powder, made water-tight, and fitted with a cork through which pass two wires to the centre of the powder. These wires are connected with a fine platinum wire. The whole arrangement is submerged in a large and strong iron mortar filled with water. When the explosion is effected, the water is thrown out of the mortar to a height of about 30 feet.

The author also refers to the idea started by Rikli (*Dingl. polyt. J.*, iii, 465), of using powder as a motive power in fire-engines.

C. L. F.

Laboratory Gasometer. By H. SEIDLER (*Zeitschr. Anal. Chem.*, xvi, 198).—A gasometer may be attached to the working-table, having a tap a few centimeters from the bottom, connected by a caoutchouc tube with the waste water-pipe. The water from the gasometer discharges itself by this tap and pipe. In order to regulate the water-pressure, it is proposed to have a large water-reservoir above the laboratory.

M. M. P. M.

A Cheap Gas Blowpipe. By FREDERICK BENTE (*Deut. Chem. Ges. Ber.*, x, 6).—An ordinary gas blowpipe is connected with a bottle of about 5 litres' capacity, provided with a cork with two holes. Through one hole passes a syphon-shaped tube, terminating inside the bottle in a Bunsen's valve, and connected outside with an ordinary india-rubber bellows. Through the other hole a tube passes directly from the gaspipe of the lamp. A very constant pressure can thus be kept up, and a very high temperature attained. The cost of the apparatus may be greatly reduced by using an india-rubber ball with a lateral aperture, which is closed with the thumb before squeezing the ball. This form, however, is not so convenient for glass-blowing.

C. L. F.

Inorganic Chemistry.

Influence of Water on the Action of Chlorine on Iodine. By G. Sodini (*Chem. Centr.*. 1876, 611).—It appears that for the reaction $I_2 + 5Cl_2 + 6H_2O = 2IHO_3 + 10HCl$ to take place, it is necessary that at least 20 parts of water to every part of iodine must be employed, otherwise iodine chloride is formed, and if the theoretical amount be employed, no iodic acid is formed at all.

E. W. P.

Solution of Sulphur in Acetic Acid. By L. Liebermann (*Deut. Chem. Ges. Ber.*, x, 866).—Sulphur dissolves to some extent in hot concentrated acetic acid; also, but very sparingly, in the dilute acid. On adding water, it is precipitated as milk, while on cooling the hot solution, or evaporating it in a vacuum, long prisms separate out.

C. S.

Preparation of some Platinum Compounds. By Julius Thomsen (*J. pr. Chem.* [2], xv, 294—300).—1. *Potassium Chloroplatinite.*—Moist chloroplatinate is brought into a syrupy consistence by addition of water; the mass is warmed; and moist cuprous chloride is added, little by little, until the greater part, but not the whole, of the chloroplatinate has dissolved. The reaction must be carried out at a temperature lower than that of the boiling point of the liquid: excess of cuprous chloride must not be added. The liquid is filtered from undissolved chloroplatinate, and allowed to cool, when the greater part of the chloroplatinite is deposited in the form of red crystals. The crystals are separated and washed with strong alcohol, until the washings cease to be coloured blue. The mother-liquor, which must be kept separate from the alcoholic washings, is evaporated at a temperature lower than that at which it boils, filtered, and allowed to cool. The second mother-liquor is mixed with strong alcohol, and a third crop of crystals of chloroplatinite thus obtained.

2. *Hydrogen Chloroplatinite.*—Prepared by decomposing a hot saturated solution of the potassium salt by means of a concentrated solution of hydrogen chloroplatinate, and filtering from precipitated potassium chloroplatinate.

3. *Ammonium Chloroplatinite.*—This salt is best prepared by decomposing a weighed quantity of the potassium salt dissolved in hot water, by a concentrated solution of hydrogen chloroplatinate, adding the proper quantity of ammonium chloride, filtering from potassium chloroplatinate, and allowing to crystallise.

4. *Platinous Hydrate.*—This hydrate is precipitated on boiling a dilute solution of potassium chloroplatinite with the necessary quantity of caustic soda in dilute solution. The hydrate is soluble in hydrobromic acid: it is reduced by dilute formic acid, with production of metallic platinum in a very finely divided condition.

5. *Potassium Bromoplatinite*, prepared by decomposing 1 mol. potassium chloroplatinite with 4 mols. sodium bromide in a boiling solution

so concentrated that the greater part of the sodium chloride which is produced separates out. The filtrate, after depositing crystals of the bromoplatinite, is evaporated down, filtered from separated salt, and again allowed to crystallise.

The bromoplatinite is recrystallised from hot aqueous solution. This salt forms large black crystals, apparently rhombic octahedrons. If prepared by rapid crystallisation, it appears as brownish-red needles. The salt is anhydrous: it undergoes decomposition similarly to the chloroplatinite.

6. *Sodium Bromoplatinate.*—A mixture of 6 mols. hydrobromic acid with a concentrated platinic chloride solution, is boiled until the hydrochloric acid is driven off; a little water and 2 mols. sodium bromide are added; and the whole is evaporated to dryness. The residue is dissolved in water: the solution deposits the pure salt with 6 mols. of water. M. M. P. M.

Chloroplatinites. By L. F. NILSON (*J. pr. Chem.* [2], xv, 260—294). The author arranges the chloroplatinites in four groups, $2RCl.PtCl_2$; $R^{ii}Cl_2.PtCl_2$; $R^{vi}{}_2Cl_6.3PtCl_2$; and $R^{iv}Cl_4.2PtCl_2$. The salts were usually produced by decomposing barium chloroplatinite with the sulphate of the metal whose chloroplatinite it was desired to produce. The free acid, $2HCl.PtCl_2$, was sometimes used.

The chloroplatinites are usually very soluble in water; they are for the most part deliquescent, and crystallise only from very concentrated solutions; but few of them are without water of crystallisation. At 100°, they are are decomposed, with production of metallic platinum, a few evolving hydrochloric acid. By evaporating their solutions in presence of hydrochloric acid, the platinum is usually partially converted into platinic chloride. The following new chloroplatinites are described.

$2RbCl . PtCl_2$: small, four-sided, red prisms, unaltered in air, easily soluble in hot water, with difficulty soluble in cold water.

$2CsCl.PtCl_2$. Long fine prisms, resembling the foregoing in its properties.

$2TlCl.PtCl_2$. Prisms of a light-pink colour, difficultly soluble in hot water.

$2LiCl.PtCl_2.6H_2O$. Dark-red four-sided prisms, with greenish lustre, resembling potassium permanganate. Easily soluble in water.

$CaCl_2.PtCl_2.8H_2O$. Thin, flexible tables; over sulphuric acid assumes a rose colour; melts at 100°, giving up 5 molecules of water, and then decomposing into chloroplatinate and platinum: very deliquescent.

$SrCl_2.PtCl_2.6H_2O$. Resembles foregoing: gives up two-thirds of its water at 100°.

$PbCl_2.PtCl_2.5H_2O$. Amorphous, red powder; decomposed slowly by boiling water.

$BeCl_2.PtCl_2.5H_2O$. Red rhombohedra: deliquesces in moist air: unchanged in dry air: gives up water and HCl at 100°. Easily soluble in water.

$MgCl_2.PtCl_2.6H_2O$. Tables, unaltered in air; give up no crystalline water at 100°.

$MnCl_2.PtCl_2.6H_2O$. Resembles the foregoing: gives up two-thirds of its water at 100°.

$CoCl_2.PtCl_2.6H_2O$. Red four- or six-sided tables: gives up 5 mols. H_2O at 100°.

$NiCl_2.PtCl_2.6H_2O$. Dark-brown tables: gives up 3 mols. H_2O at 100°.

$CuCl_2.PtCl_2.6H_2O$. Olive-brown or nearly black tables: gives up 5 mols. H_2O at 100°.

$ZnCl_2.PtCl_2.6H_2O$. Tables: gives up 6 mols. H_2O at 100°, decomposing also into chloroplatinate and platinum.

$FeCl_2.PtCl_2.7H_2O$. Dark-red prisms: gives up 5 mols. H_2O at 100°.

Cadmium chloroplatinite could not be obtained.

$Al_2Cl_6.2PtCl_2.21H_2O$. Large brilliant four-sided prisms: melts at 100°, and gives up 19 mols. H_2O.

$Cr_2Cl_6.3PtCl_2.18H_2O$. Thin, red, deliquescent prisms, giving up water and hydrochloric acid at 100°.

$Y_2Cl_6.3PtCl_2.24H_2O$. Dark-red, four-sided prisms: melts at 100°, and gives up 10 mols. H_2O.

$Er_2Cl_6.2PtCl_2.27H_2O$. Dark-red prisms; at 100° gives up 17 mols. H_2O.

$Er_2Cl_6.3PtCl_2.24H_2O$. Long four-sided prisms: loses 11 mols. H_2O at 100°.

$Ce_2Cl_6.4PtCl_2.21H_2O$. Thin four-sided prisms: loses 15 mols. H_2O at 100°.

$La_2Cl_6.3PtCl_2.18H_2O$. As the foregoing.

$La_2Cl_6.3PtCl_2.27H_2O$. Prisms: gives up 16 mols. H_2O at 100°.

$Di_2Cl_6.4PtCl_2.21H_2O$. Prisms or tables: deliquescent in air.

$Di_2Cl_6.3PtCl_2.18H_2O$. Long thin prisms.

$2ThCl_4.3PtCl_2.24H_2O$. Rhombohedrons: gives up one-fourth of its water at 100° without melting.

$ZrOCl_2.PtCl_2.8H_2O$. Large quadratic prisms.

$2HCl.PtCl_2.xH_2O$. Produced by decomposing the barium salt with the equivalent quantity of sulphuric acid, and evaporating in a vacuum. The solution, after reaching a certain degree of concentration, evolves hydrochloric acid: a dark-brown amorphous mass remains, easily soluble in water, giving up water and hydrochloric acid at 100°.

M. M. P. M.

The New Metal Davyum. By SERGIUS KERN (*Chem. News*, xxxvi, 4).—On the 28th of June, the author perceived in the residues obtained after the treatment of platinum ores in order to separate the metals of the platinum group, a new metal which he called "Davyum," in honour of Sir Humphry Davy. The ores investigated had the following average composition:—

Pt.	Ir.	Rh.	Os.	Pd.	Fe.	Ru.	Cu.	
80·03	9·15	0·61	1·35	1·20	6·45	0·28	1·02	= 100·09 p.c.

This ore was treated by the well-known Bunsen process, and in separating the rhodium and iridium, the presence of davyum was detected. The precipitate formed by the action of hydrogen at 100° was purified by dissolving it in *aqua regia*, and then treating it with chlorine in presence of barium chloride. Water was added, the barium precipitated, and filtered off, and the rhodium and iridium solutions were mixed with a concentrated solution of sodium hyposulphite. In a few days, a precipitate of a light yellow colour was obtained, which was the double sulphite of rhodium and sodium. This was filtered off, and the filtrate heated on a sand-bath in order to obtain the iridium double salt. The solution from the iridium precipitate, collected from the treatment of 600 grams of the ore, was concentrated and heated with chloride and nitrate of ammonium in excess, at 60° to 65°, for one hour. A dark-red precipitate was formed, which on ignition, gave a grey spongy mass, and when fused by means of the oxyhydrogen blowpipe, gave a silvery ingot of davyum. The weight of the ingot was 0·27 gram. Davyum dissolves readily in aqua regia, very slowly in boiling sulphuric acid. Potash gives a light yellow precipitate. Sulphuretted hydrogen in acid solutions gives a brownish precipitate, which quickly turns black when dried. With sulphocyanate of potassium it gives the same reaction as iron salts. Its specific gravity is 9·385 at 25°. It is extremely infusible, hard, and, to some extent, ductile. It may be supposed to occupy the place between molybdenum and ruthenium in Mendelejeff's periodic system of elements. Perhaps davyum is the hypothetical metal in the periodical system having the atomic weight equal to 100.

In conclusion, the author mentions that he intends to study more closely the physical and chemical properties of this metal. D. B.

Mineralogical Chemistry.

Gold from Vöröspatak. By G. vom Rath (*Jahrb. f. Min.*, 1876, 866—867).—Specimens of gold from this locality are remarkable for their fine crystallisation. The predominating forms are O and ∞O∞, often in equilibrium with occasionally 3O3, ∞O ∞O2, in combination; but the cube generally predominates. A twin-formation appears to be general, occurring even with gold in the form of "plate" and "foil." The faces of ∞O∞ are also often characterised by a fine double striation parallel to the cubical edges, also the combination-edges of ∞O∞ with O. The octohedral faces generally exhibit an equilateral striation, and depressions are sometimes observed on the cubical faces. The largest crystals found in this locality measured from 12 to 15 mm. Twins of the "middle crystal" are characterised by an abnormal development parallel to the combination-edge between O and ∞O∞, whilst twins of the form ∞O2 are curtailed in the direction of a trigonal axis, and have the appearance of a very regular obtuse hexagonal pyramid. Gold occurs also at Vöröspatak acicular, and as "wire," and the author found that what appeared to be prisms were, in reality, peculiar "penetration-twin" cubes, with ∞O2 in combination. The "plate" and "foil" formations are produced by twin formation, with an abnormal development parallel to a face of the octohedron. C. A. B.

Composition and Origin of the Diamond-bearing Sand from Du Toit's Pan, South Africa. By S. Meunier (*Compt. rend.*, lxxxiv, 250—252.)—The author having obtained several well-authenticated specimens of the diamond-bearing sand from Southern Africa, has succeeded in isolating several substances which have not been previously mentioned as occurring therein, and has been led to form an opinion concerning its origin different from that which is generally held.

From the sand were separated about eighty varieties of grains, which may be readily divided into (i) particles of rock, (ii) minerals properly so called. Among the rock-grains were noticed serpentine, a rock formed of garnet and smaragdite; another of smaragdite and ilmenite; an altered eclogite, dibasite, pegmatite, and talc-schist.

Among the minerals in isolated grains were diamond, topaz, garnet, smaragdite, bronzite, ilmenite, quartz, tremolite, asbestos, wollastonite, voalite, many zeolites, calcite, opal, red jasper, agate, iron pyrites, limonite, &c.

Geologists have unanimously agreed to assign to diamond-producing sands a deep-seated origin, an opinion which is supported by their disposition in vertical masses or layers; it has also been supposed that they owe their present position to the alteration *in situ* of pyrogenic rocks originally emitted in the form of lavas. The latter hypothesis seems to the author to be untenable in face of the list of substances given above as constituents of this variety of sand. Putting aside the more purely mineral specimens, it would seem to be impossible that so large a number of complex rocks, possessing such varying characters, could be formed under identical conditions, or produced at one and the same time in a state of mixture by the action of the same causes. He thinks it much more reasonable to suppose that each individual rock fragment has been torn from some special layer or deposit, and has afterwards been transported to the spot where the mixture actually took place.

By admitting on the one hand the deep-seated origin of diamond-bearing sand, and, on the other hand, by recognising in it the product of mechanical removal or transport, this deposit is brought into the same category as the vertically disposed granitic sands to which, under the name of "vertical alluvial deposits," the author has already directed the attention of geologists. J. W.

The Tridymite-bearing Andesite of Gerecses. By G. vom Rath (*Jahrb. f. Min.*, 1876, 869).—The andesite of the hill Gerecses, near the mountain Csik-Magos, Siebenbürgen, is grey in colour with a dense slightly shimmering "ground-mass," having an appearance like phonolite, and exhibiting here and there isolated plagioclase crystals 1—2 mm. in size. A microscopical examination revealed the presence of innumerable spots of magnetite and flat hollows (situated parallel with the stratification) enclosing beautiful tridymite crystals, not more than 1 mm. in size, but exhibiting the characteristic twin and trilling formations. A chemical examination proved the absence of phonolite. The flat druses are surrounded by a light-coloured substance which proved to be tridymite, occurring in the tile-like forms described by Zirkel. C. A. B.

Tantalite from Yancey County, North Carolina. By G. König (*Jahrb. f. Min.*, 1876, 867).—This mineral occurs in the above locality in considerable masses, the author possessing a specimen weighing a pound. Three crystal faces are recognizable, two of them being at right angles to each other, one being smooth and lustrous, whilst the other two are rough, dull, and covered with hydrated ferric oxide. Indistinct rectangular cleavage. Fracture uneven and conchoïdal. Specific gravity, 5·807. Streak black to reddish-brown. Metallic lustre. Infusible before the blowpipe. An analysis gave the following results:—

Tantalic acid	76·60	per cent.
Ferrous oxide..........	14·07	,,
Manganous oxide	0·50	,,
Magnesia	7·70	,,
	98·87	,,

The tantalite of this locality is accompanied by beryl, columbite, samarskite, and manganese-alumina-garnet. C. A. B.

The occurrence of Coelestine in Keuper-marls and its Influence upon the Constituents of Plants. By W. Stoddart (*Jahrb. f. Min.*, 1876, 867).—The coelestine in question is found near Bristol, in the lowest strata of the Keuper-marls in veins and geodes accompanied with gypsum. Crystals with a tabular "habit" and of a whitish or blue colour are found, as well as crystalline masses of a flesh-red colour. The author examined spectroscopically the ashes of plants which grow in the keuper-marls, and discovered a marked amount of strontium in them. The ash of other plants not growing on the marl, but in its immediate neighbourhood on lias-rocks, did not contain a trace of strontium. C. A. B.

Pachnolite and Cryolite. By A. Knop (*Jahrb f. Min.*, 1876, 849—854).—In 1863 the author described (*Ann. Chem. Pharm.*, cxxvii, 61) a new mineral, pachnolite, which he stated to crystallise in the rhombic system. Two varieties of pachnolite were observed, viz., A and B. The variety "A" crystallised in rather large perallelopipedic crystals whose cleavage-planes intersected at an angle of 90°, and continued apparently in the underlying cryolite. From this it might have been inferred that cryolite and pachnolite were isomorphous, but careful investigation proved it not to be the case, as the latter mineral is a hydrate of cryolite rich in calcium. Variety "B" crystallises in shining prisms. Both varieties are chemically identical, as shown by the following analysis:—

	Variety "*A.*"		*Variety* "*B.*"			
	Wöhler.	König.	Knop.	König.	v. Rath.	
Aluminium ..	13·43	13·74	13·14	12·50	13·46	12·93
Calcium	17·84	16·79	17·25	18·17	18·10	17·99
Sodium......	10·75	10·10	12·16	10·23	10·63	12·06
Water	8·20	·900	9·60	8·19	—	—
Fluorine	49·78	50·37	50·79	51·54	—	—
	100·00	100·00	102·94	100·63		

The author is of opinion that the cryolite described by Websky (*Jahrb. f. Min.*, 1867, 810) was in reality pachnolite of the variety "A," as he examined a small specimen sent to him by Websky, and found that its physical appearances coincided with those of pachnolite "A;" but its chemical composition could not be ascertained owing to the insufficiency of material for analysis. From measurements taken of the pachnolite "B" by the author and vom Rath, it appears highly probable that it crystallises in the triclinic system, but this opinion requires further confirmation owing to the difficulty experienced in the measurements of the crystals due to the strong striation observed upon the faces. From the above it would appear that pachnolite is dimorphous. C. A. B.

Henwoodite, a New Mineral. By J. H. COLLINS (*Jahrb. f. Min.*, 1876, 868).—Henwoodite occurs in globular masses having a radiating texture. Fracture, conchoïdal. Hardness, 4 to 4·45. Sp. gr., 2·67. Colour, turquoise-blue or bluish-green. Streak, white, with a light bluish-green tinge. Infusible before the blowpipe. On analysis it proved to have the following composition:—

Al_2O_3.	P_2O_5.	SiO_2.	CaO.	CuO.	Fe_2O_3.	H_2O.	Loss.	
18·24	48·94	1·37	0·54	7·10	2·74	17·10	3·97	= 100·00

This mineral is found on brown iron-ore in the West Phœnix Mine, Cornwall. C. A. B.

Enysite, a New Mineral.[*] By J. H. COLLINS (*Jahrb. f. Min.*, 1876, 868).—Occurs stalactitic in a cave at St. Agnes, Cornwall. Hardness, 2 to 2·4. Sp. gr., 1·59. Colour, bluish-green. Evolves water in matrass. Infusible before the blowpipe. Chemical composition as follows:—

SO_3.	SiO_2.	Al_2O_3.	CaO.	CuO.	CO_2.	H_2O.	
8·12	3·40	29·85	1·35	16·91	1·05	39·32	= 100·00

C. A. B.

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[*] *Note by Abstractor.*—"The so-called 'Enysite' is an *accidental secondary formation*, produced by the percolation of water through a floor upon which copper ore was stored previous to shipment. It seems, therefore, somewhat premature to give it a special name, as it appears to possess no distinctive features, and is in all probability more a mechanical mixture than a definite chemical compound."

Occurrence of Scorodite, Pharmacosiderite, and Olivenite in Greenstone. By J. H. Collins (*Jahrb. f. Min.*, 1876, 868—869.) —These minerals are found in hollows and clefts in the greenstone of the Terrace Mine, near St. Stephens, Cornwall. The scorodite is mostly found in stellar groups of very small crystals, and more rarely in rhombic pyramids of a bluish-green colour; the pharmacosiderite is found in small cubes and octohedrons of a deep-green colour; and the olivenite in tabular crystals together with scorodite.

C. A. B.

The Zeolites of the Departement Puy-de-Dome. By F. Gounard (*Jahrb. f. Min.*, 1876, 869—871).—*Natrolite* occurs the finest in Puy-de-Marman, colourless, white or reddish, in crystals 4—5 mm. in diameter, exhibiting the forms $\infty P. P. \infty P \breve{\infty}$. The crystals are found in basalt, together with small analcime trapezohedrons accompanied by arragonite and calcite. Another good locality is Tour-de-Boulade, also in basalt; the rare form $\infty P. P. \infty P \breve{\infty}. \infty P \bar{\infty}$ being found occasionally. Natrolite is also found in fresh-water limestone at Puy-de-la-Piquette accompanied by apophyllite. At Puy-de-Monton it constitutes the rind of charred wood enclosed in a basaltic conglomerate..

Mesole (thomsonite) is found in reniform masses having a fibrous radiating texture, occurring in basaltic amygdaloid at Chaux-de-Bergonne, accompanied by phillipsite and phacolite, and in basaltic hollows at Prudelles.

Phillipsite is found in basaltic amygdaloid (exhibiting the common form) attached to natrolite and accompanied by phacolite; at Puy-de-Marman, Chaux-de-Bergonne, Puy-de-la-Velle, near the village Clémensat; at Bonneval, Aubières, and, lastly, at the Cap de Prudelles, accompanied by calcite and arragonite.

Laumontite occurs only massive, of a greenish colour, accompanied by phillipsite, in the basalt of Prudelles.

Analcime is found in white, shining, or colourless trapezohedrons in basalt at Puy-de-Marman and Tour-de-Boulade near Issoire, accompanied by natrolite. It occurs in basaltic tufa at Pont-du-Château, and in hollows in phonolite at Roche-Tuillière.

Chabasite occurs in the phacolite form in basalt at Chaux-de-Bergonne, accompanied by mesole and phillipsite, and in very small twin-crystals, accompanied by natrolite at Puy-de-Marman. C. A. B.

Origin of Mineral Oils. By D. Mendelejeff (*Deut. Chem. Ges. Ber.*, x, 229).—The author, having visited the mineral oil springs in the Caucasus and in Pennsylvania, has formed a hypothesis of the origin of these oils. The view held by many, that the oil is a decomposition-product of organic remains, is rejected, chiefly on the ground that these oils are found in tertiary strata in the Caucasus, and in Devonian and Silurian strata in Pennsylvania, and must have been formed in underlying and still older strata, where but few organic remains can have existed. The author assumes, as a consequence of the condensation of the earth's substance from vapour, that the interior of the earth must consist largely of metals (iron predominating) in combination with carbon. Wherever fissures have been produced in the earth's crust by volcanic action, the water, which of necessity made its way into the interior, and thus came into contact with metallic carbides at high temperatures and pressures, must have given rise to saturated hydrocarbons, which have ascended in the form of vapour to strata where they condensed. J. R.

Galician Ozokerite, and Ceresin. By J. Grabowsky (*Pharm. J. Trans.* [3], vii, 614).—The author describes the method of mining the above minerals, and states that the best "earth-wax" or ozokerite should have a pure yellow or greenish colour; this, after having been melted, yields "a prime" earth-wax, generally used for the manufacture of "ceresin." Occasionally ozokerite is found compact and hard, melting above 100°, and dichroic (dark green in reflected, and pure yellow in transmitted light). Its composition is expressed by the formula C_nH_{2n}, and it appears to be produced by the oxidation and condensation of petroleum hydrocarbons, in the same way as naphthalene forms dinaphthyl. By supposing an oxidation of hexane and octane we obtain compounds of the formula C_nH_{2n}, which again may condense with hydrocarbons of the marsh-gas series; thus—

$$2C_8H_{18} + O_2 = C_{16}H_{32} + 2H_2O$$
$$C_{16}H_{32} + C_8H_{18} = C_{24}H_{48} + H_2O.$$

The method of separating the wax from the gangue by melting, then clarifying and casting into moulds, is described.

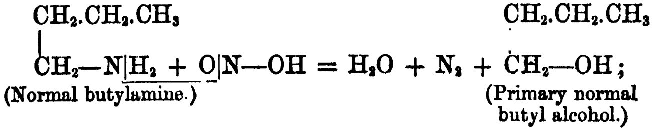
Paraffin and other hydrocarbons are prepared from ozokerite by distillation, the paraffin being pressed, treated with sulphuric acid and soda, and then filtered through animal charcoal. The best ozokerite treated with sulphuric acid and animal charcoal, yields "ceresin;" to cause it to resemble beeswax more closely, it is coloured with gamboge or alkanet. Good "ceresin" is distinguished from beeswax by not being so easily kneaded by the fingers, and by being scarcely attacked by concentrated sulphuric acid. E. W. P.

Chemical Observations on the Water of the Hot Spring at Pfäfers in Switzerland. By L. A. Buchner (*Chem. Centr.*, 1876, 455).—On comparing the analyses of the waters of the above spring made by Reichenau in 1868, and by the author, it appears that its constituents have altered in quantity, for it is found that the amount of calcium carbonate has diminished, whereas that of the magnesium carbonate, sodium sulphate, and chloride has increased. The water, moreover, appears to differ but very little from any other good spring water, temperature excepted (37·5° C.). Its source appears to be a dolomite range at a distance of about 30 miles. The analyses of the water are also given. E. W. P.

Organic Chemistry.

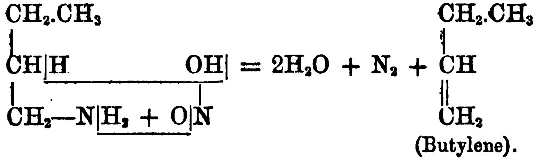
On Molecular Transformation. By V. MEYER, J. BARBIERI, and FR. FOSTER (*Deut. Chem. Ges. Ber.*, x, 130—137).—In this paper, the third of a series, the authors give the results of their experiments on normal butylamine.

Normal butylamine, when heated with nitrous acid, behaves in precisely the same manner as normal propylamine when similarly treated. A portion of the amine is converted into the corresponding alcohol, as shown in the following equation:—



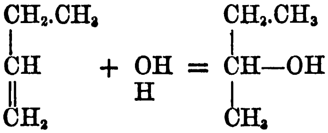
$$\underset{\text{(Normal butylamine.)}}{\begin{array}{l}CH_2.CH_2.CH_3\\ |\\ CH_2—N|\underline{H_2 + O}|N—OH\end{array}} = H_2O + N_2 + \underset{\text{(Primary normal butyl alcohol.)}}{\begin{array}{l}CH_2.CH_2.CH_3\\ |\\ CH_2—OH\end{array}};$$

but a large portion of the amine is resolved into nitrogen, water, and butylene, thus:—



$$\begin{array}{l}CH_2.CH_3\\ |\\ CH|\underline{H \qquad\qquad OH}|\\ | \qquad\qquad\quad |\\ CH_2—N|\underline{H_2 + O}|N\end{array} = 2H_2O + N_2 + \underset{\text{(Butylene).}}{\begin{array}{l}CH_2.CH_3\\ |\\ CH\\ \|\\ CH_2\end{array}}$$

Of the butylene thus formed a portion escapes in the gaseous form, whilst another portion combines with water to form secondary butyl alcohol:—



$$\begin{array}{l}CH_2.CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} + \begin{array}{l}OH\\ H\end{array} = \begin{array}{l}CH_2.CH_3\\ |\\ CH—OH\\ |\\ CH_3\end{array}$$

J. R.

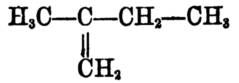
Preliminary Researches on the Action of Magnesium on some Organic Compounds. By SERGIUS KERN (*Chem. News*, xxxv, 117).—Magnesium in powder acts very strongly on most organic compounds. It gives a very energetic reaction with chloroform and a small quantity of water, with evolution of methane:—$2CHCl_3 + 3H_2O + 6Mg = 2CH_4 + 3MgO + 3MgCl_2$. On iodoform and bromoform it acts in a similar way. With an alcoholic solution of $C_2H_2Br_4$, magnesium yields acetylene dibromide when allowed to act in the cold, but on heating acetylene is obtained:—(1.) $C_2H_2Br_4 + Mg = C_2H_2Br_2 + MgBr_2$. (2.) $C_2H_2Br_4 + 2Mg = C_2H_2 + 2MgBr_2$. Propylene bromide, with addition of water and magnesium, evolves pure propylene, $C_3H_6Br_2 + Mg = C_3H_6 + MgBr_2$. Magnesium acts very readily on ethyl bromide with addition of H_2O and C_2H_6O, forming a compound C_2H_5MgBr, which yields $MgBr_2$ and $(C_2H_5)_2Mg$. In presence of water only, the C_2H_5MgBr gives hydrated oxybromide of magnesium, and ethane, C_2H_5; C_2H_5MgBr yields, with ethyl alcohol, in absence of water. C_2H_5OMgBr, and ethane; on C_2H_5I magnesium acts similarly.

All the above reactions require a low temperature, not exceeding 30—40°, and in some cases even lower. Magnesium ethyl, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Mg$, is easily obtained by the action of magnesium powder on ethyl iodide; if slowly oxidised, this compound is converted into magnesium ethylate, $\left.\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\right\}Mg$

Magnesium-ethyl forms a better means of obtaining other organic compounds than zinc-ethyl, many compounds of the alcohol radicles with metals being prepared in a very pure state by this reagent.

D. B.

Amylene. By A. WISCHNEGRADSKI (*Chem. Centr.*, 1876, 595).—Commercial liquid amylene is only half soluble in sulphuric acid; water and alkalis convert the resulting sulphamylic acid into dimethylethyl carbinol. The hydrocarbons contained in the liquid and unattacked by the sulphuric acid, consist of isopentane (amyl hydride) mixed with about 20 per cent. of a pentene convertible by HI and $Pb(OH)_2$ into methyl-propyl carbinol, $CH_3—CHOH—C_3H_7$, as proved by the study of its properties, and of its oxidation-product. Consequently, this hydrocarbon is identical with the ethyl-allyl of Wurtz, or with the methylethylethene, $CH_3.CH{=}CH.CH_2.CH_3$, obtained by Saytzeff and Wagner from diethyl carbinol. If the amylene of Flawitzky, boiling at 25°, is treated with HI in the cold, and afterwards with argentic or plumbic oxide, tertiary amyl alcohol is obtained, and not, as Flawitzky expected, methylisopropyl carbinol. Upon these grounds the author does not consider amylene to be isopropyl-ethylene, but to have the structure—



$$\begin{array}{c}H_3C—\underset{\underset{\displaystyle CH_2}{\|}}{C}—CH_2—CH_3\end{array}$$

F. J. L.

Constitution of Amylene. By F. FLAWITZKY (*Deut Chem. Ges. Ber.*, x, 230).—The author finds that amylglycol from amylene prepared by the action of alcoholic potash on amyl iodide (the latter obtained from amyl alcohol of fermentation), when oxidised with potassium bichromate and sulphuric acid in the proportion indicated by the equation—

$$C_5H_{12}O_2 + O_4 = (CH_3)_2CH.COOH + CO_2 + 2H_2O,$$

yields chiefly isobutyric acid. At the same time a small quantity of an oily liquid boiling at 60—65°, and smelling of acetone, is formed.

The isobutyric acid in this experiment must obviously be derived from an amyl-glycol having the constitution $(CH_3)_2CH.CHOH.CH_2OH$, and this in turn must have been derived from isopropylethylene, $(CH_3)_2CH.CH{=}CH_2$, whilst the formation of acetone is due to the decomposition of isobutyric acid.

J. R.

Some Products of the Action of Red Fuming Nitric Acid on Coal Gas. By T. Akestorides (*J. pr. Chem.* [2], xv, 62—64).—By passing coal gas through red fuming nitric acid, the author finds that oxalic acid is formed, besides nitrobenzene, nitrotoluene, &c. On afterwards experimenting with pure products, he found that benzene, toluene, and xylene, each in vapour, and mixed with carbonic acid or hydrogen, and passed through red fuming nitric acid, gave the following results. From benzene, oxalic acid was never obtained, but from toluene and xylene it was. Both hydrocarbons give nitro-derivatives as well as oxalic acid. The ethene present in coal-gas will doubtless also suffer partial conversion into oxalic acid by oxidation with nitric acid. The author has tried this experiment with pure ethene, and obtained a rich yield of oxalic acid. The reaction is analogous to that of potassium permanganate on ethene noticed by Berthelot.

On long standing and repeated shaking, almost all the ethene was absorbed by the nitric acid. A portion seems to be oxidised to carbon monoxide, the greater portion passing into oxalic acid:—

$$C_2H_4 + O_5 = H_2O + C_2O_4H_2$$
$$\text{and}\quad C_2H_4 + O_4 = 2CO + 2H_2O.$$

The wide-spread notion that oxalic acid is easily decomposed by nitric acid is without foundation; it is, on the contrary, very stable in presence of this acid.

(On experimenting with the petroleum gas from the gas-works of Prof. Hirzel, the author obtained a good yield of pure oxalic acid. It is possible this fact may prove technically useful.)

The gas experimented with above was from Leipzig, and in the manufacture of it Westphalian and Zwickau coals, mixed with Bohemian lignite, were used. W. S.

Sulphuryl Chloride, and its behaviour to Alcohols. By Paul Behrend (*J. pr. Chem.* [2], xv, 23—42).—The recognition of numerous and interesting analogies between the *carbonyl*-derivatives and the *sulpho*-derivatives, has already excited repeated comparative researches in relation to the question, "What degree of parallelism exists between the radicles carbonyl (CO) and sulphuryl (SO_2) as exhibited in their compounds?"

The first effort of the author was directed to the obtaining of sulphuryl chloride in larger quantities, and the existing methods not allowing of this, a new method was devised to compass this end. Pure sulphuryl oxychloride, easily prepared by the action of hydrochloric acid gas on sulphur trioxide, was heated in sealed tubes to 200—210° for a day in a paraffin bath. The product was now distilled, and the portion passing over below 110° was redistilled on the water-bath. At about 70° nearly pure sulphuryl chloride distils over. To free it from small quantities of oxychloride and sulphur trioxide, the whole is now poured upon a funnel filled with pieces of ice. The oxychloride is thus decomposed at once, and so is the sulphur trioxide, the sulphuryl chloride being scarcely affected, and sinking as an oily layer

to the bottom of the vessel. This oil is separated and dried in the exsiccator over phosphoric pentoxide. It is then distilled once more on the water-bath, the first few drops being rejected. Thus a pure product was obtained. The reaction is

$$2SO_2(OH)Cl = SO_2Cl_2 + SO_2(OH)_2.$$

The yield by this method is very good, about 40 per cent. of the calculated quantity being obtained. The author states that he cannot confirm the observation of Williamson, that the boiling point of sulphuryl oxychloride is not to be relied on, on account of this body splitting up on repeated distillation into sulphuric acid and sulphuryl chloride. He finds that the body boils constantly at 153°, and is not decomposed, either by distillation in a retort with inverted condenser for a day, or by passing through a tube containing pumice-stone and heated to low redness. It is decomposed at higher temperatures only, in sealed tubes. Sulphuryl chloride gradually decomposes in presence of water, yielding sulphuric acid and hydrochloric acid:—

$$SO_2Cl_2.2H_2O = 2HCl + SO_2(OH)_2.$$

Dubois found that sulphuryl chloride, treated with benzene and phenol respectively, gave rise to the following reactions:—

$$C_6H_6 + SO_2Cl_2 = C_6H_5Cl + HCl + SO_2$$
$$C_6H_5.OH + SO_2Cl_2 = C_6H_4Cl.OH + HCl + SO_2.$$

The author has studied the action of sulphuryl chloride on alcohols, and finds that in this action it closely resembles carbonyl chloride.

The reactions take place in two stages. First, only one chlorine atom of the sulpho-chloride is disturbed, bodies of the general formula, $SO_2{<}\begin{smallmatrix}OX\\Cl\end{smallmatrix}$, being formed (X signifies a univalent organic radiclo). These bodies, on fresh exposure to the action of the chloride, are capable of forming compounds in which both chlorine-atoms are replaced, giving rise to neutral sulphuric ethers.

I. *Action of Sulphuryl Chloride on Ethyl Alcohol.*—In order that the analogy between the chlorides of sulphuryl and carbonyl should hold good, only one of the two chlorine-atoms in the sulpho-compound should be at first replaced. This is really the case, and as Williamson predicted, chlorosulphuric ether, $SO_2(OC_2H_5)Cl$, is formed. Experiment proved also that only one of the chlorine-atoms in sulphuryl chloride is replaced when this body and alcohols react upon each other. This action is quite analogous to that which takes place with carbonyl chloride. The following equation illustrates this reaction:—

$$Cl_2SO_2 + C_2H_5.OH = \underset{\text{Ethyl chloro-sulphate.}}{SO_2(OC_2H_5)Cl} + HCl.$$

By passing ethene into sulphuryl oxychloride, Max Müller obtained a body of like percentage composition, but different properties; this body is evidently therefore an isomeride.

Action of Water on Ethyl Chlorosulphate.—This is illustrated as follows:—

$$SO_2(OC_2H_5)Cl + H_2O = SO_2(OC_2H_5)OH + HCl.$$

Ethylsulphuric acid.

Only slight action results from treatment with ice-water, but on shaking for a long time with water at the ordinary temperature everything gradually dissolves to a strongly acid liquid, *ethylsulphuric acid.*

II. *Action of Sulphuryl Chloride on Methyl Alcohol.*—This action is more powerful than that on ethyl alcohol; results similar—

$$SO_2Cl_2 + CH_3.OH = SO_2(OCH_3)Cl + HCl.$$

Methyl chlorosulphate.

Ethyl chloro-sulphate can be distilled undecomposed only in a vacuum. Methyl chlorosulphate decomposes, with separation of carbon, a little over 100°. The distillation was therefore effected in a rarefied atmosphere, obtained by filling the vessel with carbon dioxide and then absorbing by potash. By this method a mercurial column was obtained in the manometer tube of 700 to 710 mm. in height. The distillation was now effected at 80°, when about two-thirds of the fluid passed over, but the thermometer never remained stationary, and the residue was charred to a spongy mass.

Methyl chloro-sulphate decomposes in presence of water at ordinary temperatures, just like ethyl chlorosulphate, yielding hydrochloric acid and methylsulphuric acid; but so much heat is developed in consequence of the vigorous action taking place, that the methylsulphuric acid easily passes into methyl alcohol and sulphuric acid. The decomposition must therefore be conducted slowly and in the cold.

III. *Sulphuryl Chloride and Isobutyl Alcohol.*—The reaction proceeds with far less vigour than in the two preceding cases, II and I.

The isobutyl chlorosulphate decomposes at ordinary temperatures, gradually becomes resinous, and is converted into a dark brown sticky mass. At 80° this change occurs instantaneously.

Isobutyl chloro-sulphate is a clear colourless liquid, not nearly so strongly attacked by water as the two preceding chlorosulphates, and not smelling so strongly.

The body is formed as follows:—

$$SO_2Cl_2 + C_4H_9.OH = SO_2(OC_4H_9)Cl + HCl.$$

Isobutyl chlorosulphate.

With water it decomposes as follows:—

$$SO_2(OC_4H_9)Cl + H_2O = SO_2(OC_4H_9)OH + HCl.$$

Isobutyl-sulphuric acid.

IV. *Sulphuryl Chloride and Benzyl Alcohol.*—If benzyl alcohol be dropped into an equivalent proportion of sulphuryl chloride, tolerably strong action commences, hydrochloric acid escapes, and a liquid is formed of a somewhat pungent aromatic odour, but far more unstable than the isobutyl chlorosulphate. A pure product could not be obtained, as formation of a resinous mass so quickly set in.

Behaviour of Ethyl Chlorosulphate to Ethyl Alcohol.—Reaction sets in easily in the cold. Purgold represented this as follows:—

$$SO_2(OC_2H_5)Cl + 2C_2H_5.OH = (C_2H_5)_2O + H_2SO_4 + C_2H_5Cl.$$

This the author proves to be an incorrect representation, as ethyl chloride is not to be found in the escaping gases. The oily liquid obtained is neutral and odourless, and decomposes instantaneously in presence of water. The equation is therefore corrected to the following—

$$SO_2(OC_2H_5)Cl + C_2H_5.OH = SO_2(OC_2H_5)_2 + HCl.$$

Ethyl chlor-sulphate. Diethyl sulphate.

This reaction points significantly to the analogy between the two bodies, $SO_2(OC_2H_5)Cl$ and $CO(OC_2H_5)Cl$, for the reaction—

$$CO(OC_2H_5)Cl + C_2H_5.OH = CO(OC_2H_5)_2 + HCl$$

also holds good.

Ethyl Chlorosulphate and Methyl Alcohol.—Action same as in above case with ethyl alcohol.

$$SO_2(OC_2H_5)Cl + CH_3.OH = SO_2(OC_2H_5)(OCH_3) + HCl.$$

Methyl-ethyl sulphate.

This ether cannot be distilled without decomposition, even in a vacuum. It is miscible in all proportions with alcohol.

On treatment with water, diethylic sulphate yields ethyl-hydrogen sulphate and ethyl alcohol—

$$SO_2(OC_2H_5)_2 + H_2O = SO_2(OC_2H_5)(OH) + C_2H_5.OH.$$

It was interesting to see if ethyl-hydrogen sulphate, methyl-hydrogen sulphate or a mixture, arose on treating the mixed ether with water. What actually occurs is as follows:—

$$SO_2(OC_2H_5)_2(OCH_3) + H_2O = SO_2(OC_2H_5)OH + CH_3.OH.$$

Methyl Chloro-sulphate and Ethyl Alcohol.—The following reaction occurs:—

$$SO_2(OCH_3)Cl + C_2H_5.OH = SO_2(OCH_3)(OC_2H_5) + HCl.$$

Decomposed by water the mixed ether yields methyl-hydrogen sulphate and methyl alcohol.

It thus appears that the mixed ether, $SO_2(OCH_3)(OC_2H_5)$ last obtained is not isomeric, but identical with that obtained as above, by the action of ethyl chloro-sulphate on methyl alcohol.

Ethyl-butyl sulphate and methyl-butyl sulphate were also prepared. They suffer a remarkable decomposition in presence of water.

Ethyl-butyl sulphate was prepared from ethyl chlorosulphate and butyl alcohol. On standing in the air it gradually acquires a brown colour. It decomposes instantaneously with water.

$$SO_2(OC_4H_9)(OC_2H_5) + H_2O = SO_2(OC_4H_9)OH + C_2H_5OH.$$

Methyl-butyl sulphate, prepared from methyl chlorosulphate and butyl alcohol, reacts neutral, is without odour, and is decomposed by water just like the preceding.

A glance at the three following decompositions by water will show that the alcohol-radicles richest in carbon remain behind to form acid compounds or ethers, whilst those poorest in carbon go forth, unite with hydroxyl and form alcohols.

These researches show then that the analogy existing between the action of sulphuryl- and carbonyl-chlorides on alcohols is very close:—

*1. $SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl$
$COCl_2 + 2H_2O = CO(OH)_2 + 2HCl.$

2. $SO_2Cl_2 + C_2H_5.OH = SO_2(OC_2H_5)Cl + HCl$
$COCl_2 + C_2H_5.OH = CO(OC_2H_5)Cl + HCl.$

3. $SO_2(OC_2H_5)Cl + C_2H_5.OH = SO_2(OC_2H_5)_2 + HCl$
$CO(OC_2H_5)Cl + C_2H_5.OH = CO(OC_2H_5)_2 + HCl.$

W. S.

Researches on Crude Wood Spirit. By G. KRÆMER and M. GRODZKI (*Deut. Chem. Ges. Ber.*, ix, 1920—1927).—The detection of the higher fatty acids among the products of the distillation of wood points to the occurrence of the ketones homologous with acetone, as acetone is formed from two molecules of acetic acid, so must aldehyde and the ketones be regarded as arising from the action of formic acid, acetic acid, propionic acid, &c., on each other.

Aldehyde formed by the action of formic acid on acetic acid is seldom found in large quantities in wood spirit. The greater part is taken up by the methyl alcohol with formation of dimethyl-acetal, which from the nearness of its boiling point to that of methyl alcohol has generally escaped notice, but which is nevertheless a constant constituent of wood spirit. Acetone is found in much larger quantities than aldehyde. Methyl-ethyl ketone (boiling-point 80° to 85°) is another constant product, and is formed from propionic acid. The higher ketones, together with allyl alcohol, are found in the peculiarly smelling oil which passes over last during the distillation. The allyl alcohol may be removed by shaking up with water, and the ketones may be extracted by sodium bisulphite. The ketone described by Claisen (*Berichte*, viii, 1258) which boiled at 129° to 131°, and gave a solid compound with sodium bisulphite, must have been a condensed

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* *Note by Abstractor.*—The equations given are—

$$SO_2Cl_2 + H_2O = SO_2(OH)_2 + HCl$$
$$\text{and } COCl_2 + H_2O = CO(OH)_2 + HCl.$$

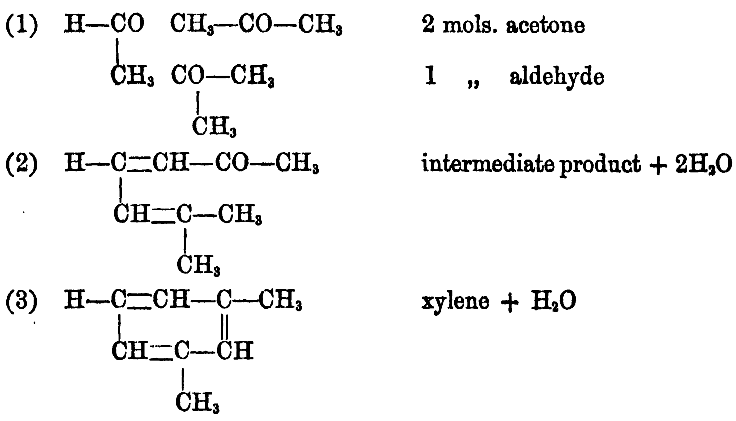
Evidently each equation lacks 1 mol. H_2O, and 1 mol. HCl, and should be as above corrected.

ketone, consisting perhaps of C_6H_8O. The oily portions which dissolve with difficulty or not at all in sodium bisulphite, were next examined. Fractional distillation led to no definite results: a number of portions were obtained from 110° to over 180°. Two fractions, one collected between 130° and 140°, and the other between 165° and 175°, were submitted to further examination. Analyses led to the empirical formulæ, $C_8H_{12}O$ and $C_{10}H_{16}O$, but these were not confirmed by the vapour-densities.

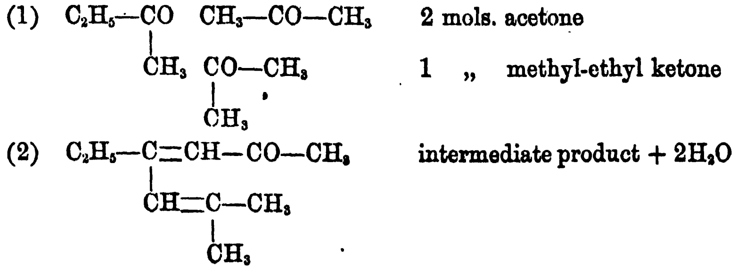
Treatment with bromine and bromine-water gave no satisfactory results. Oxidising agents converted the substances chiefly into acetic and carbonic acids, but a part suffered further condensation, and by treating this with zinc chloride and sulphuric acid, and drying over sodium, a body was obtained from No. II which proved to be cymene, while No. I (boiling at 134° to 140°) when similarly treated yielded xylene. When No. II was acted on by sulphuric acid without the previous treatment with zinc chloride, an oil was obtained which was not pure cymene, but contained in addition a hydrocarbon boiling above 300°. Analysis of this body led to the formula $C_{10}H_{14}$, indicating that a partial polymerisation of the cymene had taken place.

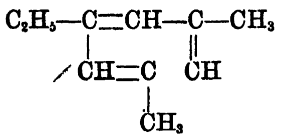
The following scheme gives the views of the authors as to the origin of these hydrocarbons:—

I.



II.



(3)  , cymene + H_2O

Hence the xylene must be isoxylene, and the cymene the dimethylethylbenzene analogous to mesitylene. This was confirmed by the oxidation-products—the former yielding isophthalic, the latter mesitylenic acid. The ketone of Cahours' corresponding with toluene must have been derived from two molecules of aldehyde and one of acetone, and his cumol (the ketone corresponding with mesitylene) from three molecules of acetone.

The authors are investigating the intermediate products above mentioned. G. T. A.

Action of Sodium Mercaptan on Iodomethane, Methene Iodide and Chloroform. By PETER CLAESSON (*J. pr. Chem.* [3], xv, 174—176).—Carius gave 58·8—59·5° and 132—133·5° as the boiling points of methyl-ethyl sulphide and ethyl-amyl sulphide produced by the action of ethyl disulphophosphate on methyl and amyl alcohol respectively, and stated that both were oxidised by nitric acid to ethylsulphuric acid. Saytzeff showed that in the case of the ethyl-amyl sulphide the product of this reaction was $\genfrac{}{}{0pt}{}{C_2H_5}{C_5H_{11}}>S<\genfrac{}{}{0pt}{}{OH}{O.NO_2}$. The author has therefore prepared the methyl-ethyl sulphide by the action of sodium mercaptan on iodomethane in alcoholic solution, and obtained amyl boiling at 64°, and having a specific gravity 0·837 at 20°; this oil (methyl-ethyl sulphide) when oxidised by nitric acid, yields a colourless syrup, soluble in water, and having the composition $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}>SO<\genfrac{}{}{0pt}{}{OH}{O.NO_2}$, which is analogous to Saytzeff's nitrate of ethylamylsulphuric oxide, and changes when decomposed by barium carbonate into an oil of the composition $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}>SO$.

The action of sodium mercaptan on methene iodide or chloroform is similar to that which it exerts on methyl iodide or carbon tetrachloride, the chlorine or iodine being replaced by the group $S.C_2H_5$. Disulphethyl-methane, or methene mercaptide, a colourless oil boiling at 184°, sp. gr. 0·987 at 20°, and yielding by oxidation ethylsulphonic acid, has been obtained by a process similar to the foregoing; as also has trisulphethyl-methane or methyl trimercaptide, which by oxidation yields ethylsulphonic acid. Methyl-ethyl sulphide is therefore the only sulphethyl derivative of methane which does not form ethylsulphonic acid on oxidation, as Carius stated. E. W. P.

Bromoform. By ERNST SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 193).—The specific gravity of bromoform is, according to Löwig, 2·13, and according to Cahours, 2·90 at 12°. These statements differing widely, the author has determined the specific gravity of pure bromoform boiling at 149—150°, which he finds to be 2·775 at 14·5°.

J. R.

Ethyl Mercaptan. By PETER CLAESSON (*J. pr. Chem.* [2], xv, 193—218).—Crude ethylsulphate of sodium, obtained by neutralising a mixture of sulphuric acid and alcohol with sodium carbonate, was evaporated, and after the sodium sulphate had crystallised out, the mother-liquor containing sodium ethylsulphate was mixed with potassium sulphide and gently heated for 12 hours in a retort, the vapour which escaped being condensed in caustic potash. From 1 litre of alcohol and 350 grams of potassium hydrate, 280—290 grams of crude mercaptan were obtained, containing 70—80 per cent. of mercaptan, the remainder being ethyl sulphide. It was purified by shaking with dilute caustic potash and distillation over mercuric oxide, and separated from ethyl sulphide by conversion into the sodium compound.

A compound of mercaptan with water is always formed when the mixed vapours are passed through a condenser, the temperature of the water being 8° or less. This substance consists of small needles, and is stable if kept at a temperature of 12° or 14° in a stoppered bottle. It is insoluble both in water and mercaptan, and has the formula $C_2H_5.SH + 18H_2O$.

Sodium and *potassium mercaptides* may be prepared, either by dissolving the metal in mercaptan, when the compound separates out in white masses resembling snow, or better, by dissolving potassium or sodium in absolute alcohol and adding mercaptan, drop by drop, or passing mercaptan vapour into the alcoholate. With water, sodium mercaptide decomposes into sodium hydrate and mercaptan, and with excess of alcohol into sodium alcoholate and mercaptan. The latter reaction, however, is by no means so complete. An aqueous solution of potash or soda dissolves mercaptan, partially converting it into mercaptide, and great contraction of the solution ensues. Both mercaptan and the mercaptides of the alkali-metals are powerful reducing agents; nitrobenzene, for example, is reduced by them to azobenzene. Sodium mercaptide absorbs oxygen when the gas is passed through an alcoholic solution, ethyl disulphide being formed. The action is different, however, when dry oxygen is passed over dry sodium mercaptide heated to 100—120°. The mercaptide does not alter its appearance, but after solution in water and neutralisation of the free alkali with carbonic acid, and evaporation to dryness, alcohol extracts from the residue a very deliquescent, indistinctly crystalline salt of the formula $C_2H_5.SO_2Na$—*sodium ethylsulphinate.* The zinc salt of this acid is identical with that which Wischin obtained by passing sulphurous anhydride through a solution of zinc-ethyl in ether. No ethyl-sulphonic acid is formed. Sodium mercaptide may be heated to 200° in gas which has no action on it, without decomposition. From a very strong solution in alcohol it crystallises in indistinct needles. On treatment with dilute acid, the mercaptan separates as an oil; it may thus be freed from ethyl sulphide; the alcoholic solution of sodium mercaptide is evaporated to dryness, water is added, and the solution separated from ethyl sulphide either by filtration or agitation with benzene. The mercaptan is then separated from the residue by addition of dilute acid.

When added to metallic salts, mercaptan and its compound with sodium act in a manner precisely analogous to sulphuretted hydrogen and ammonium sulphide.

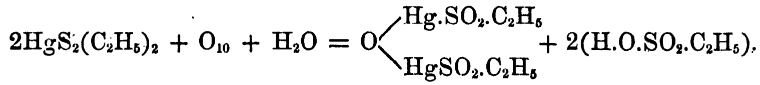
Thallium mercaptide, $Tl.S.C_2H_5$, prepared by shaking thallious carbonate with mercaptan; it is a yellow curdy precipitate.

Ferrous mercaptide, $FeS_2(C_2H_5)_2$. Mercaptan reduces ferric to ferrous salts; but an alcoholic solution of ferric chloride, when mixed with excess of mercaptan and then with ammonia, gives a black shiny precipitate of ferrous mercaptide. It decomposes below 100°.

Nickel, and Cobalt mercaptides, $NiS_2(C_2H_5)_2$ and $CoS_2(C_2H_5)_2$. The nickel-compound is chocolate-coloured; both are obtained by addition of mercaptan to a solution of a salt of the metal, best the acetate.

Zinc, and cadmium mercaptides, $ZnS_2(C_2H_5)_2$ and $CdS_2(C_2H_5)_2$. Precipitated from their compounds with weak acids; they dissolve in dilute acids without decomposition, and are reprecipitated on neutralisation of the acid. They are white, indistinctly crystalline bodies, and are best prepared from the acetates. They dissolve in ammonia, and are reprecipitated on neutralisation.

Mercuric mercaptide. Best prepared by shaking mercuric cyanide with mercaptan. It crystallises out in long very thin crystals. On application of heat the mercaptide melts to an oil, devoid of smell and taste. On treatment with warm nitric acid, a basic mercuric ethylsulphonate is formed, thus:



$$2HgS_2(C_2H_5)_2 + O_{10} + H_2O = O\begin{cases} Hg.SO_2.C_2H_5 \\ HgSO_2.C_2H_5 \end{cases} + 2(H.O.SO_2.C_2H_5).$$

This reaction is quantitative.

Mercaptides of metals of the platinum group:—

Palladium mercaptide. A yellow powder, stable up to a dull red heat, when it decomposes, with evolution of so much heat that the palladium melts. *Rhodium mercaptide:* yellow precipitate of the formula $Rh_2S_6(C_2H_5)_6$. Mercaptan has no action on salts of iridium, ruthenium, or osmium, except to reduce them; it might thus be used for separating platinum from iridium.

Tin mercaptide, $Sn.S_4(C_2H_5)_4$. Stannic chloride, dissolved in carbon disulphide, is mixed with a solution of mercaptan in the same solvent; the mercaptide remains as a thick oil after the solvent has been removed by distillation. Water does not attack it in the cold, but on heating it the tin separates as oxide. On distillation, ethyl disulphide is formed, metallic tin remaining, but in a vacuum the tin mercaptide may be distilled. It does not solidify at −40°. It may also be prepared by treating a strong solution of stannic chloride in water with mercaptan.

Bismuth mercaptide, $BiS_3(C_2H_5)_3$, is one of the most characteristic of the mercaptides. It is obtained by mixing a solution of a salt of bismuth with mercaptan, in long flexible yellow needles. It is soluble both in alcohol and in ether, and crystallises from these solvents in needles. It melts at 79°, oxidises easily in air, and when strongly heated decomposes into bismuth and ethyl sulphides.

Arsenic mercaptides. Arsenious chloride acts on mercaptan at the ordinary temperature, but even at 100° no higher compound than $As(S.C_2H_5)_2Cl$ is formed. The tri-mercaptide is best obtained by dissolving arsenious chloride in ether, and adding sodium mercaptide, keeping the former in excess. The excess is afterwards removed by a current of dry ammonia. After filtration, and distillation of the ether, the product is quite free from chlorine. Both these products are colourless oils with a bad smell; the former when heated gives metallic arsenic, arsenic chloride, and ethyl disulphide; and the latter metallic arsenic, and ethyl disulphide. The former reacts with water, giving arsenious and hydrochloric acid and mercaptan, but is not oxidised by air; while the latter is not acted on by water, but decomposes in air, arsenious acid being formed.

Antimonious chloride forms a compound with mercaptan of the formula $SbCl_3.C_2H_5SH$, which is decomposed by water.

Phosphorous chloride and mercaptan do not act on each other when cold: when heat is applied the chlorine is exchanged for the group C_2H_5S, but this exchange is not thorough, unless the mixture is heated to 100°. The behaviour of phosphorous chloride resembles that of the arsenic compound.

Carbon mercaptides. Carbon compounds containing a haloïd element exchange it for the group $C_2H_5.S$. The more carbon the substance contains the slower is the action; *e.g.*, methyl iodide forms methyl-ethyl sulphide much more easily than amyl iodide yields amyl-ethyl sulphide, and CCl_4 is more easily attacked than C_2Cl_6. 1st. *Carbon tetramercaptide.* This compound is best prepared by dissolving sodium in absolute alcohol and adding successively the theoretical amounts of mercaptan and carbon tetrachloride, both dissolved in alcohol. The mixture begins to boil and sodium chloride separates out. Water is then added, and the mixture distilled, the last portions of the distillate rejected. The mercaptide thus obtained is an oil with a peculiar smell, and a specific gravity of 1·01. It cannot be distilled alone. It is oxidised by fuming nitric acid to carbonic and ethylsulphonic acids.

Dicarbon hexmercaptide, $C_2(SC_2H_5)_6$. Obtained from carbon hexchloride. At very low temperatures it becomes solid.

Dicarbon tetramercaptide, $C_2(SC_2H_5)_4$. From sodium mercaptide and tetrachlorethene at 100°, the mercaptide crystallises in rhombohedrons like calcspar; it dissolves in ether, and melts at 54°.

Sulphur mercaptides, or Ethyl polysulphides. Ethyl tetrasulphide, $(C_2H_5)_2S_4$, is obtained by mixing solutions of sulphur chloride and mercaptan in carbon disulphide. After removal of carbon disulphide and excess of mercaptan by distillation, it remains as a light-coloured oil, heavier than water, with an extremely disagreeable smell, soluble in carbon disulphide and in ether, but very sparingly in alcohol.

Its action on the metals is, as a general rule, to convert them into sulphides. It converts potassium cyanide into the sulphocyanate, and with caustic potash gives the thiosulphate. On distillation alone it decomposes into sulphur, and the disulphide, and with water it gives the trisulphide and sulphur. On heating it to 150° with sulphur, the latter is dissolved; possibly the pentasulphide is formed. W. R.

Ethyl-sulphinic Acid. By PETER CLAESSON (*J. pr. Chem.* [2], xv, 222—224).—The method of preparation of this acid has been described in the preceding abstract. Its sodium salt is very deliquescent, and crystallises from absolute alcohol in masses of needles. When left to itself it appears to decompose partially, according to the equation—

$$2(C_2H_5)NaSO_2 = (C_2H_5)_2S + Na_2SO_4.$$

By oxidation with nitric acid, the acid and its salts yield ethylsulphonic acid, ethylsulphone, and sulphuric acid. With chloracetic ether the following reaction takes place:

$$C_2H_5NaSO_2 + CH_2Cl.CO.OC_2H_5 = C_2H_5SO_2.CH_2.CO.OC_2H_5 + NaCl.$$

The ether, after treatment with water and saponification, gives an acid oil of the formula $C_2H_5S.CH_2.CO.OH$; it is ethyl sulphacetic acid.

With bromine, ethylsulphuric acid gives the bromide of ethylsulphonic acid, which smells like mustard-oil. With barium hydrate the acid gives barium ethylsulphonate, and with tin and hydrochloric acid, mercaptan. Iodine attacks the salt, but the resulting liquid iodide is difficult to purify. W. R.

Synthesis of Diallylcarbinol. By ALEX. SAYTZEFF (*Liebig's Annalen*, clxxxv, 129—148).—Attempts to prepare triallylcarbinol by acting on carbonic ether with zinc and ethyl iodide, and decomposing the resulting mass with water, led to the production of little but diallyl; when, however, formic ether was employed, there was produced about twice as much diallylcarbinol as of diallyl; propylene was also set free, but only in small quantities. From 661 grams of ethyl formate, and 2994 of ethyl iodide, about 150 grams of crude diallyl (boiling at near 65°), and 350 of crude diallylcarbinol (boiling, 145—160°) were obtained; after fractional distillation and perfect dehydration, the latter boiled at 151° (corrected). With alcohol and ether diallylcarbinol is miscible in all proportions; in water it is almost insoluble; its specific gravity is 0·8758 at 0°, 0·8644 at 12°, and 0·8478 at 32°; by continued boiling it partially splits up into water and a hydrocarbon, C_7H_{10}, the latter being apparently polymerised, and yielding a small residue of high boiling point. When it was dissolved in ether or carbon disulphide, and treated with the requisite amount of bromine, *diallycarbinol tetrabromide* was formed; this could not be distilled without decomposition, and did not yield any pentatomic alcohol on treatment with oxide of lead or silver. When, however, *diallylcarbinol acetate* was formed (by treating the carbinol with acetic anhydride at 160° in a sealed tube), and the product was heated with bromine, and the resulting tetrabromide heated for a long time with silver acetate and glacial acid, the pentacetate of the alcohol, $C_7H_{11}(OH)_5$, $C_7H_{11}(O.C_2H_3O)_5$ was formed; and on saponifying this with alcoholic hydrochloric acid, an anhydride of the alcohol itself was produced, $C_7H_{11}\left\{\begin{matrix}O\\(OH)_3\end{matrix}\right.$. Diallycarbinol acetic ether boils at 169·5° (corrected), and has the specific gravity 0·919 at 0°, 0·902 at 17·5°; the tetrabromide does not solidify in a freezing mixture.

Diallylcarbinol chloranhydride (monochlorheptine), $C_7H_{11}Cl$, is formed when pentachloride of phosphorus acts on the carbinol; it boils between 140° and 145°, but appears in so doing to lose the elements of hydrochloric acid and become partially converted into the hydrocarbon, C_7H_{10} (heptone), or a polymeride of higher boiling point; this hydrocarbon is readily formed, along with its polymerides, by the action of alcoholic potash on the chloranhydride. It boils at 115°, and readily combines with six proportions of bromine, forming $C_7H_{10}Br_6$; this compound, being presumably indicated by the formula, $CH_2Br—CHBr—CHBr—CHBr—CH_2—CHBr—CH_2Br$, is probably the hexbromhydrin of a hexatomic alcohol, and may possibly by suitable treatment enable a homologue of mannite to be formed.

On oxidation with potassium dichromate and sulphuric acid, diallyl carbinol gave rise to formic acid and carbon dioxide; no acetic acid was produced, and nothing else could be isolated from the product of the reaction; whence it results that the structure of the allyl groups in the carbinol is $CH_2{\equiv}CH—CH_2—$, and not $CH_3—CH{\equiv}CH—$, since in the latter case acetic acid must have been formed; hence, and from its mode of genesis, the formula of the carbinol must be—

$$CH_2{\equiv}CH—CH_2—CH.OH—CH_2—CH{\equiv}CH_2.$$

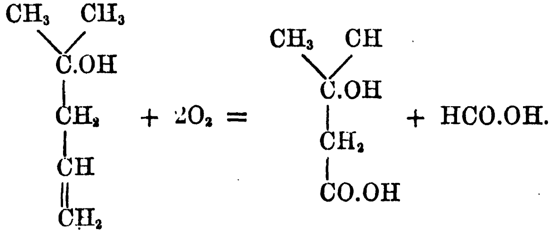
C. R. A. W.

Action of a Mixture of Ethyl and Allyl Iodides on Ethyl Formate in presence of Zinc. By J. KANOUNIKOFF and A. SAYTZEFF (*Liebig's Annalen.*, clxxxv, 148—150). From the results detailed in the previous extract, and the production of methyl-ethyl carbinol by the action of a mixture of methyl and ethyl iodides on zinc and formic ether, it would seem probable that a mixture of ethyl- and allyl-iodides would give rise to ethyl-allyl carbinol; on trying the experiment, however, only diallyl carbinol, identical with that just described, was formed, boiling at 148—151°, and agreeing therewith in physical characters, in the acetic ether, and in the products of oxidation. C. R. A. W.

Synthesis of Allyldimethyl Carbinol. By MICHAEL and ALEXANDER SAYTZEFF (*Liebig's Annalen*, clxxxv, 151—169).—By acting on 1 molecule of acetone with 1 of ethyl iodide in presence of a large excess of zinc, and decomposing with water, a considerable quantity of allyldimethyl carbinol is formed, about 250 grams of crude product, boiling at 115—125°, being obtained from 350 of acetone and 1000 of allyl iodide. After fractionation, the carbinol forms a transparent, slightly viscid liquid, of camphoraceous odour, boiling at 119·5° (corrected), and combining with water to form a hydrate, $C_6H_{12}O,H_2O$, which boils at 116—117°, without perceptible decomposition. The specific gravity of the carbinol is 0·8438 at 0°, 0·8307 at 18°; it readily combines with bromine, forming a dibromide, which does not solidify in a freezing mixture, and cannot be distilled; heated with acetic anhydride to 150° in a sealed tube, it forms *allyldimethylcarbinyl acetate*, boiling at 137·5° (corrected), and having the specific gravity 0·9007 at 0°, 0·8832 at 18·65°; this also combines with bromine, forming an easily decomposible liquid dibromide, insoluble in water, but readily dissolved by ether and carbon disulphide.

Phosphorus pentachloride converts the carbinol into *allyldimethyl carbinol chloranhydride* (monochlorhexene), $C_6H_{11}Cl$, boiling at 109—114°; treatment with alcoholic potash converts this into a hydrocarbon (hexine), C_6H_{10}, boiling at 80°, and combining with four proportions of bromine, like its isomeride diallyl; the tetrabromide is, however, liquid, whilst diallyl tetrabromide is a solid crystalline body.

On oxidation by potassium dichromate and sulphuric acid, allyldimethyl carbinol gives rise to acetone, carbon dioxide, and acetic acid, with excess of oxidising agent; to formic acid, and *oxyvalerianic acid*, with lesser quantities, the reaction in the latter case being—



Oxyvalerianic acid is obtained by agitating the oxidation products with ether, and distilling off the ether from the extract thus gained; it forms a brownish, thick syrup, which does not crystallise, even when purified and rendered quite colourless by conversion into lead salt, and treatment with sulphuretted hydrogen, and finally into silver salt, recrystallisation, and treatment with sulphuretted hydrogen. The silver salt crystallises well, and is anhydrous, $C_5H_9AgO_3$; the copper, barium, calcium, and zinc salts are anhydrous, after drying over sulphuric acid; the calcium salt is apt to form a gummy mass, in which crystallisation ensues but slowly; the lead salt does not crystallise: these salts were obtained by neutralising the acid with the respective metallic carbonates. In order to obtain the best yield of oxyvalerianic acid, 50 grams of allyldimethylcarbinol, 196 potassium dichromate, 325 sulphuric acid, and 1960 of water should be employed; the carbinol is mixed with one-half of the solution obtained by dissolving the potassium dichromate in the water; to the other half of this solution the sulphuric acid is added, and the resulting liquid allowed to drop slowly into the other solution by means of a stoppered receiver, with frequent agitation for 48 hours; the whole is then warmed on the water-bath for some hours, and after cooling, treated with ether.

C. R. A. W.

Synthesis of Diallylmethyl Carbinol. By B. SOROKIN (*Liebig's Annalen*, clxxxv, 169—175).—By acting on acetic ether with zinc and 2 molecules of allyl iodide, *diallylmethyl carbinol* is formed. After purification this boils at 158·4° (corrected), and has the specific gravity 0·8638 at 0°, 0·8523 at 16°. It forms an acetic ether by treatment with acetic anhydride at 150°, boiling at 177·3° (corrected), and having the specific gravity, 0·8997 at 0°, 0·8872 at 15°; with bromine both the carbinol and its acetate combine, forming very unstable tetabromides, which cannot be obtained pure, owing to decomposition. By oxidation the carbinol forms acetic acid and carbon dioxide, with a trace of a non-volatile acid, giving an insoluble silver salt, but produced in too small quantity for investigation. C. R. A. W.

Action of Electrolytic Oxygen on Glycol. By AD. RENARD (*Compt. rend.*, lxxxiv, 352—353).—The effects were observed in the same manner as with glycerin (this Journal, 1875, 1249, and 1876, ii, 64). 10 grams of glycol, diluted with 100 c. c. of water acidulated with a twentieth of sulphuric acid, were submitted to the action of a current produced by 4 Bunsen cells. Hydrogen was evolved at the negative pôle, and at the positive pole, a mixture containing 5 p. c. CO_2, 57·15 p. c. CO, and 37·85 p. c. O.

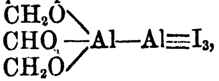
After allowing the action to continue for 36 hours, the liquor is neutralised with calcium carbonate, and filtered. The filtrate distilled yields a solution of glyceric aldehyde, identical with that obtained in the same manner from glycerin (1876, ii, 64). The residue of the distillation, evaporated on the water-bath, forms a syrup, which, when treated with alcohol, yields a deposit of calcium formate and glycollate. Another portion of the original liquor left to spontaneous evaporation, with pieces of potash under a bell-jar, becomes a thick liquid, which, when mixed with water and saturated with calcium carbonate, yields (on evaporating the filtrate) crystals of calcium glycollate.

The alcoholic liquid resulting from the precipitation of the calcium salts, contains a glucose identical in character with that obtained by the electrolysis of glycerin.

In the electrolysis of glycol neither oxalic acid nor glyoxal is formed. F. D. B.

Action of Aluminic Iodide on Glycerin. By W. R. H. (*Chem. News*, xxxv, 237).—It has been shown by Gladstone and Tribe, that the principal end-product of the action of aluminium and iodine on alcohol is the same as the product from the action of phosphorous iodide, namely, ethyl iodide, the intermediate product, aluminic iodo-ethylate, $Al_2\left\{\begin{matrix}(C_2H_5O)_3\\ I_3\end{matrix}\right.$, splitting up at a high temperature into ethyl iodide and aluminic oxide. The action of the aluminium-iodine couple was tried on mono- and di-ethylin, when it was found that the action is very energetic, and the products somewhat numerous. It was therefore thought better to study in the first place the action of aluminium iodide on glycerin. Glycerin heated for some time to expel water, was heated in a retort with aluminium foil, and iodine gradually added. At 200° an oily liquid containing iodine passed over, which was washed with and separated from water, dissolved in alcohol, and shaken with mercury, with which it combined, with heat-evolution, to a yellow body soluble in warm alcohol, from which the mercury allyl-compound thus formed separated on cooling in brilliant, nearly white scales, rapidly turning yellow, and consisting of mercuric allyl-iodide, C_3H_5HgI. The alcohol from which the mercury compound was precipitated gave no precipitate when mixed with water, showing absence of isopropyl iodide. The end reaction of Al_2I_6 on $C_3H_5(HO)_3$ may therefore be thus shown:—

$$2C_3H_5(OH)_3 + Al_2I_6 = 2C_3H_5I + Al_2O_3 + 3H_2O + 2I_2,$$

corresponding with the phosphorus iodide reaction. It is probable that an intermediate body,  $\left.\begin{array}{l}CH_2O\\CHO\\CH_2O\end{array}\right\rangle Al{-}Al{\equiv}I_3$, analogous to $(C_2H_5O)_3Al_2I_3$, may be formed, and destroyed again by the high temperature. If in the distillation a reversed condenser were used, it might be possible to form isopropyl iodide by the further action of HI. In the above experiment, however, the allyl iodide was distilled off as fast as formed. 40 grams of iodine gave about 45 to 48 of crude allyl iodide.

D. B.

Glycerin Derivatives. By HANRIOT (*Bull. Soc. Chim.* [2], xxvii, 256—258).—The author first prepared glyceric monochlorhydrin. Glycerin, dried at 200° and saturated with dry hydrochloric acid gas, was heated for 100 hours on the water-bath in a sealed flask. At the end of that time the liquid consisted of monochlorhydrin and excess of glycerin. It was then distilled, first on the water-bath until the distillate no longer showed an acid reaction, and afterwards over a naked flame at a pressure of several centimeters, those portions being collected which passed over between 130° and 170°. After several rectifications the monochlorhydrin distilled over at 159° under a pressure of 10 centimeters of mercury. It was necessary to be very careful not to apply the naked flame to the retort whilst any free acid remained, as in presence of hydrochloric acid glycerin and monochlorhydrin unite to form polyglycerins.

The monochlorhydrin thus prepared was a thick, colourless, neutral liquid, soluble in all proportions in water, alcohol, and ether. It had a density of 1·338 at 0°, and distilled without alteration under a pressure of 10 centimeters of mercury at 159°.

One part of monochlorhydrin was now added to a solution consisting of one part of potassium cyanide in three parts of water; the mixture became hot, and after cooling crystals of potassium chloride separated. The supernatant liquid was mixed with hydrochloric acid, heated for six hours, and evaporated on the water-bath. By means of alcohol, a substance was extracted from the residue which after repeated rectification proved to be a thick yellowish liquid having a strong acid reaction. It corresponded to the formula $C_4H_8O_4$.

This acid furnishes difficultly crystallisable salts.

The sodium salt crystallises in prisms containing water of crystallisation. It is very soluble in water and in alcohol, but not in ether.

The potassium salt is less soluble in alcohol than the sodium salt, and it crystallises less easily. These two salts are obtained by decomposing the barium salt with the corresponding sulphates.

The barium salt is a solid mass of the consistence of gum arabic, obtained by the addition of alcohol to a solution of barium carbonate in the free acid. It is anhydrous.

The zinc salt is obtained by saturating the free acid by oxide of zinc; it is insoluble in alcohol, and does not crystallise.

H. H. B. S.

Metallic Glycerides. By J. Puls (*J. pr. Chem.* [2], xv, 83—105).—Various metallic oxides are dissolved by aqueous solutions of glycerin containing caustic potash, the amount of oxide dissolved being in many cases proportionate to the commonly accepted molecular weight of that oxide. Ferric oxide is dissolved by glycerin containing potash, when these three substances are mixed in the proportions of 1 : 3 : 1 molecules (a solution of ferric chloride was used). From such a solution the ferric chloride is slowly but completely precipitated on standing. The more the solution is diluted with water the more quickly is the ferric oxide thrown down. By increasing the proportion of glycerin, a more stable solution is obtained. No change is noticeable in a liquid containing glycerin, ferric oxide, and potash in the proportion of 12 : 1 : 1 molecules.

When these three substances are mixed in the proportion of 3 : 2 : 1 molecules, a solution is obtained which almost instantly becomes gelatinous; by doubling the amount of potash the liquid remains in an ungelatinised state for 6 hours or so.

The author believes that these solutions contain a colloïdal modification of ferric oxide. Many substances bring about the pectisation of clear solutions of ferric oxide in glycerin and potash: of these the most energetic is potassium sulphate. Finely powdered fluorspar, calcspar, heavy spar, &c., cause the same phenomenon. In experiments with cupric oxide the author shows that the greater the amount of water present, the amount of potash remaining constant, the less is the amount of oxide dissolved, but that by increasing the amount of potash the aqueous glycerin is able to hold in solution a much larger quantity of oxide. An aqueous solution of glycerin containing 3·66 p.c. of the latter substance, dissolved 79·3 parts of cupric oxide (= one molecule) for each 92 parts of glycerin (= one molecule), when 6 molecules of potash were present for each molecule of glycerin. A solution of glycerin in dehydrated alcohol containing 1·97 p. c. of glycerin, is capable of dissolving one molecule of cupric oxide per molecule of glycerin, when 4 molecules of potash are added to the liquid.

Solutions of cupric oxide in glycerin are not altered by addition of potassium sulphate, nor of those substances which cause solutions of ferric oxide in the same solvent to gelatinise. Cupric oxide is thrown down from an alcoholic glycerin solution after the liquid has remained for some time in a well stoppered vessel.

It is possible to determine, with tolerable accuracy, the amount of glycerin in solutions containing from 1·85 to 5·80 p. c. of that compound. An increased volume of copper solution—preferably of cupric chloride—is added, then such a quantity of potash solution as shall ensure the presence of one molecule of potash over and above the quantity required to unite with the chlorine of the cupric chloride for each molecule of copper oxide added. If no precipitate is produced, a further quantity of copper solution is added; the liquid is filtered, and the copper is determined in a portion of the filtrate. For each molecule of glycerin (= 92) present, provided the total amount neither falls below 1·85 p. c., nor exceeds 5·80 p. c., 73·5 parts of cupric oxide are dissolved.

The behaviour of aqueous solutions of glycerin containing potash, towards several other metallic oxides, is described.

Barium, strontium, and calcium oxides are dissolved in the proportion of one molecule BaO to 5 and to 6 molecules of $C_3H_8O_3$; one molecule of SrO to 10—20 molecules of $C_3H_8O_3$; and one molecule of CaO to 22—34 molecules of $C_3H_8O_3$. The author did not succeed in isolating compounds of these oxides with glycerin, in the manner described by Chevreul.

The formation of mono-sodium glycerate, $C_3H_7NaO_3$, by the action of sodium amalgam melting at 30° upon glycerin, washing with amylic and finally with pure ethylic alcohol, is described. Attempts were made to prepare other metallic glycerates. A solution of the sodium compound in methylic alcohol was acted upon by a solution of cupric chloride in the same solvent: the results pointed to the production of a compound in which sodium was replaced by copper, but it was found impossible to separate this body from excess of cupric chloride upon which it appeared to react, with production of complicated compounds.

All attempts to prepare a sodium derivative of glycerin in which more than one atom of hydrogen was replaced by metal, led only to negative results. M. M. P. M.

Grape-sugar. By M. HÖNIG and M. ROSENFELD (*Deut. Chem. Ges. Ber.*, x, 871—873).—On adding sodium ethylate to a solution of grape-sugar in absolute alcohol a bulky precipitate of $C_6H_{11}NaO_6$ is formed, which by quickly filtering on the pump, washing with alcohol, pressing, and drying over sulphuric acid, is obtained as a friable powder, which is very hygroscopic, and easily decomposed by water. On heating it in a current of hydrogen at 100°, it loses two molecules of water, and is converted into a brown, spongy mass. Alcoholic bromine produces bromoform, and the known compound, $C_6H_{12}O_6 + NaBr$, while a solution of bromine in bromoform seems to form substitution-products. C. S.

Transformation of the Crystallisable Sugar of Brown Sugar into Inactive Glucose. By W. GAYON (*Compt. rend.*, lxxxiv, 606—609.)—Recent observations have shown that the reduced glucose contained in brown sugar is inactive to polarised light. This glucose varying in quantity in different sugars, it appeared interesting to find whether it varied in the same sample at different times. Experiments show that it does, there being at the same time a loss of crystallisable sugar. This conversion of crystallisable into uncrystallisable sugar is greater during the summer than during the spring, being therefore augmented by heat; whilst moisture also favours the change. The importance of these facts upon the package and transport of moist sugars is evident. F. J. L.

Composition of Gun-Cotton. By P. CHAMPION and H. PELLET (*Compt. rend.*, lxxxiv, 609—611).—A sample of dry gun-cotton was analysed, and gave: free cellulose, 1·00 per cent., dinitrocellulose 6·00 per cent., and by difference 93 per cent. of a substance which the authors consider to be pentanitrocellulose, and not, as maintained by Abel, trinitrocellulose.

This substance gave the following figures, which are compared with those calculated for pentanitrocellulose:—

	Calculation.	Analysis.
C	26·54	26·18
H	2·79	2·81
N	12·51	12·78
O	58·16	58·23

F. J. L.

A Saccharine Matter obtained from the Leaves of the Walnut. By TANRET and VILLIERS (*Compt. rend.*, lxxxiv, 393—396).—By an appropriate treatment of 1 kilogram of dry walnut leaves, the author obtained 3 grams of a saccharine matter to which he proposes to give the name of *nucite.* This substance crystallises in small, well-defined, colourless clinorhombic prisms. They contain water of crystallisation, and are efflorescent, very soluble in water, and insoluble in alcohol, ether or chloroform. The solution of nucite does not deviate the plane of polarisation, is not fermentable by yeast, and does not reduce Fehling's liquid. Nucite is not oxidised by dilute nitric acid into nucic, or into oxalic acid; but the product of the reaction is an unstable substance which has not yet been examined. The crystals of nucite, which have a very sweet taste, correspond in composition with the formula, $C_6H_{12}O_6 + 2H_2O$. R. R.

Note on the Synthesis of the Aldehydes. By C. GÖTTIG (*Deut. Chem. Ges. Ber.*, x, 8—10).—With respect to the small yield given by the method for obtaining ethyl-salicylic aldehyde from ethyl-iodide and sodium-salicylic aldehyde (Perkin, *Chem. Soc. J.*, xx, 422 [1867], it was deemed advisable to see if the method of preparing the aldehyde from the acid by distillation of the calcium salt with calcium formate, applied also to aldehydes which distil without decomposition. It is true this method has been already employed by Piria (*ibid.*, 100—104), for the preparation of benzoic, cinnamic, and anisic aldehydes; by Limpricht (*Ann. Chem.*, xcvii, 368), for the reduction of acetic acid to acetic aldehyde; and by other chemists for the synthesis of other aldehydes, but not yet for the production of the aldehyde of a polyatomic acid. It has been employed by the author successfully in the formation of ethyl-salicylic aldehyde, but attempts to produce salicylic aldehyde in a similar manner have not yet succeeded.

Experiment 1. Equal weights of pure dry calcium formate and calcium ethylsalicylate, prepared as already described in *Deut. Chem. Ges. Ber.*, ix, 1474, were distilled on a sand-bath in lots of 10 grams each. A yellow oil came over between 246—249°, the boiling point of Perkin's ethyl-salicylic aldehyde, which, on analysis, yielded numbers corresponding with the formula $C_6H_4\left\{\begin{matrix}OC_2H_5\\ COH\end{matrix}\right.$. Although the H was slightly too high (unavoidable where such small quantities are employed), yet the result of the CO_2 determination leaves no doubt of its identity with the ethylsalicylic aldehyde prepared by Perkin, especially as the similarly constituted anisic aldehyde (methyl-para-oxybenzoic aldehyde) was formed in this way by Piria (*Cimento*, iii, 126).

2. An attempt to obtain salicylic aldehyde by the distillation of a mixture of calcium salicylate and calcium formate, was not successful. An oil came over, which proved to be chiefly phenol, and crystallised out in the neck of the retort. Whether a mixture of the two salts in different proportions would give different results remains to be proved.

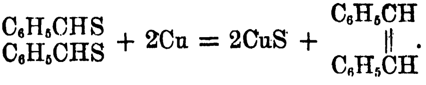
C. L. F.

On Thialdehydes. By H. Klinger (*Deut. Chem. Ges. Ber.*, ix, 1893—1896).—*Thiacetaldehyde.*—The colourless oil which is produced by the action of sulphuretted hydrogen on an aqueous solution of acetaldehyde, has, according to Pinner (*Berichte* iv, 257), the formula $C_2H_4O + C_2H_4S$. This is converted by acids into a solid, to which Hofmann assigns the formula $C_6H_{12}S_3$. The author is led by his experiments in converting the one into the other, to the conclusion that the first of these formulæ is incorrect, and that the oily substance consists of a thialdehyde $(CH_3CHS)_n$, with which possibly traces of an oxy-mercaptan, $CH_3CH\begin{matrix}SH\\ OH\end{matrix}$, are mixed.

When trithiacetaldehyde is heated on the water-bath with acetyl- or benzoyl-chloride, it is converted into a new polymeric modification, which crystallises from glacial acetic acid in fine white needles, with a melting point of 125° to 126°. If benzoic acid is substituted for the chloride, a new thiacetaldehyde is produced, which melts at 145° to 150°, and is easily soluble in ether, hot benzene, alcohol, chloroform, and acetic acid. It can easily be volatilised with steam. It forms two compounds with silver nitrate, $C_6H_{12}S_3.AgNO_3$, and $C_6H_{12}S_3.3Ag.NO_3$; the latter of these crystallises in fine nacreous plates, the first in compact, colourless needles. They are both soluble in boiling alcohol, though with difficulty; when heated, they detonate sharply. Acetic acid acts in a similar manner to the chlorides on long-continued heating. When the trimolecular thiacetaldehyde, dissolved in toluene, is treated with sodium, a small quantity of a new polymeric thiacetyaldehyde is formed, together with resinous products, potassium (?) sulphide, and a combustible gas which seems to consist chiefly of ethylene. Sulphuretted hydrogen forms, with alcoholic solution of aldehyde, a body different from the oil described by Weidenbusch and Pinner; it has not yet been fully examined.

Thiobenzaldehyde is obtained by passing dry sulphuretted hydrogen into an alcoholic solution of bitter almond oil. It consists, according to the concentration of the solution, of amorphous, faint-red flocks, or of a reddish oil, which quickly solidifies. Thiobenzaldehyde volatilises at 83—85°, is decomposed on further heating, and is very soluble in benzene and chloroform, but with some difficulty in hot alcohol.

Its composition is $C_6H_5.CHS$. This body is polymerised by acid chlorides in the same way as thiacetaldehyde. The polymeric thiobenzaldehyde $(C_6H_5CHS)_n$, which is obtained from the amorphous variety, consists of brilliant white needles: these crystals melt at 225—226°, and undergo decomposition. They are easily soluble in hot acetic acid, less easily in alcohol, benzene, and chloroform. Silver and mercury compounds have not yet been successfully prepared. Amorphous thiobenzaldehyde, when heated with finely-divided copper, is decomposed according to the equation—



$$\begin{matrix}C_6H_5CHS\\C_6H_5CHS\end{matrix} + 2Cu = 2CuS + \begin{matrix}C_6H_5CH\\ \| \\C_6H_5CH\end{matrix}.$$

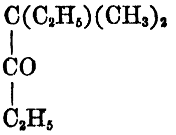
Stilbene.

By treating acetone in water with sulphuretted hydrogen, an oily body is obtained, which cannot be distilled without decomposition. The author is investigating this body. Sulphuretted hydrogen seems to have little if any action on benzophenone.

G. T. A.

On an 8-carbon Pinacolin.

By LAWRINOWITSCH (*Bull. Soc. Chem.* [2], xxvii, 265).—The author has obtained a pinacolin of the formula $C_8H_{16}O$ from methylethylacetone by first converting it into the corresponding pinacone, $C_8H_{18}O_2$. By oxidation, acetic acid and dimethylethylacetic acid, $C(CH_3)_2(C_2H_5)COOH$, are formed, indicating its structure to be :—



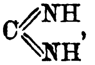
$$\begin{matrix}C(C_2H_5)(CH_3)_2\\ | \\CO\\ | \\C_2H_5\end{matrix}$$

This pinacolin, which is a liquid boiling at 145—150°, is identical with that which Wischnegradsky obtained by the action of zinc-ethyl upon the chloranhydride of dimethyl-ethylacetic acid.

H. H. B. S.

Constitution of Cyanamide.

By M. FILETI and ROBERT SCHIFF (*Deut. Chem. Ges. Ber.*, x, 425—429).—The authors' experiments on this subject lead them to conclude that, of the two alternative formulæ for cyanamide—

$NC—NH_3$ and ,

the latter is untenable.

Action of Chloral on Cyanamide.—When equal numbers of molecules of these substances are mixed together, the mixture becomes hot and a colourless syrup is formed, which, if left to itself, undergoes no further change; but on heating it in the water-bath, the liquid suddenly swells up to some 20 times its bulk, and solidifies in a yellowish-white fibrous mass, which falls to powder with the slightest pressure.

The compound thus formed is soluble in alcohol, ether, and chloroform, and is left, on evaporating the solutions, in the form of a viscid resinous mass, which hardens in the air. After washing with water, the compound is quite stable. It turns brown at 210° without undergoing decomposition. Its composition, as determined by analysis, agrees with the formula $(CN)_3[NH-CH(OH)CCl_3]_3$, which the authors regard as the true formula of the substance. The syrup first formed probably contains a compound formed by the simple union of chloral with cyanamide, which, like most other derivatives of cyanamide, becomes polymerised by heat, thus yielding a substituted melamine.

Conversion of Cyanamide into Diethylcyanamide.—When diargentic cyanamide is heated over the water-bath for some hours with excess of ethyl iodide, silver iodide is deposited. The red filtrate was divided into two portions, and treated as follows:—

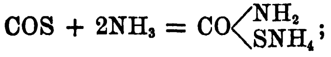
1. One portion was submitted to distillation, and yielded a distillate boiling at 186° (uncor), and giving, on analysis, numbers agreeing with the formula of diethylcyanamide, $NC-N(C_2H_5)_2$.

2. The other portion was mixed with excess of hydrochloric acid, and evaporated to dryness, when it yielded a mixture of ammonium chloride and diethylamine hydrochloride, a reaction of diethylcyanamide previously observed by Cloez and Canizzaro.

Inasmuch as the diethylcyanamide from which the diethylamine was obtained in the last reaction was prepared directly from cyanamide, it seems pretty certain that the two hydrogen-atoms in cyanamide are in combination with the same nitrogen-atom; and accordingly the true formula of cyanamide is $NC-NH_2$. J. R.

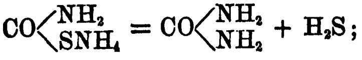
Action of Carbon Oxysulphide on Aqueous Ammonia. By Ernst Schmidt (*Deut. Chem. Ges. Ber.*, x, 191—193).—When carbon oxysulphide is passed into strong aqueous ammonia, it is largely absorbed, the solution acquiring a faint yellow colour. On evaporating the still strongly alkaline liquid in glass basins, ammonium carbonate and hydrogen sulphide escape and urea is left in crystals.

This formation of urea, &c., is preceded by that of ammonium oxysulphocarbamate; for when carbon oxysulphide is passed into aqueous ammonia cooled to 0°, the solution gives at first no precipitate with baryta-water, and no coloration with lead paper; but after a time both these reactions occur. Hence, it appears that 1 mol. of carbon oxysulphide unites with 2 mols. of ammonia, as shown by the equation—

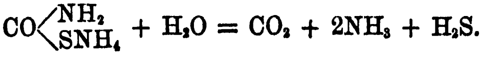


$$COS + 2NH_3 = CO\genfrac{\langle}{}{0pt}{}{NH_2}{SNH_4};$$

and that the ammonium-oxysulphocarbamate thus formed breaks up in the following ways:—



$$CO\genfrac{\langle}{}{0pt}{}{NH_2}{SNH_4} = CO\genfrac{\langle}{}{0pt}{}{NH_2}{NH_2} + H_2S;$$



$$CO\genfrac{\langle}{}{0pt}{}{NH_2}{SNH_4} + H_2O = CO_2 + 2NH_3 + H_2S.$$

The former of these decompositions takes place almost exclusively when ammonia saturated with carbon oxysulphide in the cold is at once agitated with lead hydrate or carbonate, so that on evaporating the filtrate, a considerable quantity of urea is left behind. J. R.

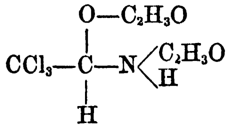
Constitution of Chloral-ammonia and Aldehyde-ammonia.

By Robert Schiff (*Deut. Chem. Ges. Ber.*, x, 165—171).—The author prepares chloral-ammonia as follows:—Anhydrous chloral is dissolved in 1½ times its weight of dry chloroform; the solution is cooled in ice; and a rapid current of ammonia is passed into it, till the whole suddenly solidifies. The mass is then thrown upon a vacuum filter, to free it from chloroform, washed with ether, and spread on paper to dry. The product thus obtained is nearly pure. It is a dazzling white body, nearly insoluble in water, and sparingly soluble in ether and chloroform. It melts at 62—64°.

Action of Acetyl Chloride or Acetic Anhydride on Chloral-ammonia.—When either of these substances is poured upon chloral-ammonia, the mixture becomes hot, and a clear solution is formed, which, on cooling, or on addition of water, solidifies to a white crystalline mass. The product crystallises from hot water in fine rhombic tables, which melt at 156°, and dissolve in alcohol, but not in ether. Its composition agrees with the formula, $C_2H_3Cl_3NO,C_2H_3O$ (*monacetyl-chloral-ammonia*).

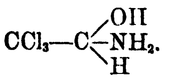
Action of Acetyl Chloride on Monacetyl-chloral-ammonia.—These substances do not react further in the cold, but when they are heated to 120° in sealed tubes, a clear solution is formed, which on cooling deposits a white crystalline mass. This mass dissolves in ether and in glacial acetic acid, and crystallises from the latter in large, transparent prisms, melting at 117—118°, and dissolving sparingly in alcohol, but easily in ether. Analysis of the crystals shows them to have the formula, $C_6H_8O_3NCl_3$, which is that of a diacetyl-chloral-ammonia.

In hot water this substance undergoes instant decomposition, the water taking up acetic acid, whilst monacetyl-chloral-ammonia, melting at 155°, is deposited. Hence it appears that the two acetyl-groups in the body have different functions, the second evidently having taken the place of hydrogen in hydroxyl, the presence of which in chloral-ammonia is thus demonstrated. The constitution of the dichloracetyl-compound must, therefore, be expressed thus:—



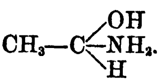
$$\begin{array}{c} O-C_2H_3O \\ | \\ CCl_3-C-N\!\begin{matrix}C_2H_3O\\H\end{matrix} \\ | \\ H \end{array}$$

consequently chloral-ammonia and its analogue, aldehyde-ammonia, must be represented by the following formulæ:—



$$CCl_3-C\!\begin{matrix}OH\\NH_2.\\H\end{matrix}$$

Chloral-ammonia.



$$CH_3-C\!\begin{matrix}OH\\NH_2.\\H\end{matrix}$$

Aldehyde-ammonia.

J. R.

Melamine Sulphocyanate. By AD. CLAUS (*Deut. Chem. Ges. Ber.*, ix, 1915—1916).—This compound is formed by heating ammonium sulphocyanate quickly up to 250°, and maintaining this temperature, till the whole mass becomes solid. The interspaces of the crude melam thus produced are filled with a fine white sublimate, in the form of small prisms, which can be dissolved out by warm water. On cooling the solution, prismatic crystals, generally of a faint, yellowish colour, are deposited, which are soluble in alcohol, and may be sublimed without change by careful heating. The formula of melamine sulphocyanate is $C_3N_6H_6.CNSH$. G. T. A.

Formation of Allyl Sulphocarbimide. By ERNST SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 187).—Gerlich showed that by the action of allyl bromide on potassium sulphocyanate at 0°, allyl sulphocyanate alone is produced, but that this product when heated is at once transformed into the isomeric allyl sulphocarbimide (mustard-oil).

The author has examined the action of myrosin (filtered extract of white mustard) on calcium myronate, at 0°, with the object of determining which of the isomerides is thus formed. He finds that the product consists chiefly of allyl sulphocarbimide, but that a small quantity of allyl sulphocyanate is also formed. J. R.

The Action of Alkaline Sulphocyanates upon the Hydrochlorides of the Alkaloïds of the Fatty Series. By P. DE CLERMONT (*Bull. Soc. Chim*, [2], xxvii, 198, 199).—It is a well known fact that the hydrochlorides of the alkaloïds of the aromatic series are decomposed by the action of alkaline sulphocyanates and water at 100° into sulpho-ureas. The sulphocyanate passes into the corresponding isomeric sulpho-urea. The author endeavoured to convert the sulphocyanates of the alkaloïds of the fatty series into sulpho-ureas, but did not succeed. He boiled hydrochloride of ethylamine with an aqueous solution of potassium sulphocyanate, evaporated to dryness, and dried the residue for some time at 100° C., and afterwards dissolved it in water, obtaining by this treatment crystallised sulphocyanate of ethylamine. This substance is very deliquescent; gives the blood-red reaction with ferric salts, but so far has not been converted into its isomeride, ethyl-sulpho-urea. Sulphocyanate of amylamine was also prepared, but it could not be converted into the corresponding sulpho-urea, whence it seems to be impossible to convert sulphocyanates of the fatty series into the corresponding sulpho-ureas. The author made some further experiments to ascertain whether this molecular change was caused by the presence of ammonium or potassium chloride, and found that they did not exert any influence. C. A. B.

Oxidation of Oxy-acids. By N. LEY (*Deut. Chem. Ges. Ber.*, x, 230).—The author, from the results of his own investigations and those of other chemists, deduces the following law of oxidation of the secondary oxy-acids of the α-series (*i.e.*, hydroxy-acids, in which the secondary alcohol-group, CHOH, is united directly to the carboxyl-group). Under the influence of oxidising agents these acids are broken up in such a manner that their carboxyl yields carbon dioxide and water, whilst the residue ($C_nH_{2n+1}.CHOH$) is converted into an aldehyde, and ultimately into the corresponding acid. Thus, ethylidenelactic acid yields carbon dioxide, water, aldehyde, and acetic acid, α-Oxybutyric acid (from monobromobutyric acid) yields carbon dioxide, propyl aldehyde, and propionic acid. Isopropyl-oxyacetic acid yields by oxidation with potassium bichromate and sulphuric acid, carbon dioxide, isobutyl aldehyde, and isobutyric acid.

The author has examined also the following hydroxy-acids:—

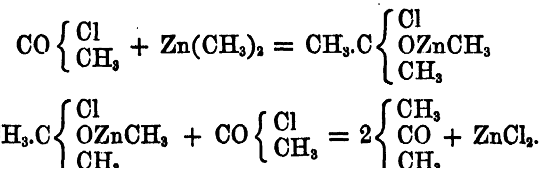
1. An acid obtained by the action of hydrochloric and hydrocyanic acids on valeral, melting at 54—55°. This acid yields by oxidation carbon dioxide, an acid of the formula $C_5H_{10}O_2$, and valeral.

2. Oxycaproic acid (probably $CH_3.CH_2.CH_2.CH_2.CHOH.COOH$), obtained from caproic acid of fermentation, crystallising in laminæ which melt at 57°. It forms silver, zinc, cadmium, and barium salts, which are very sparingly soluble, and are deposited from their solutions in the amorphous state. By oxidation it likewise yields carbon dioxide, an aldehyde, and a valeric acid.

3. Oxyheptylic acid, from normal heptylic acid, crystallises from ether in transparent laminæ, and from water in needles, which melt at 65°. It yields by oxidation, carbon dioxide, an aldehyde, and a caproic acid.

J. R.

Action of Organo-zinc Compounds on the Chlorides of Acid Radicles. By D. PAULOFF (*Bull. Soc. Chim.* [2], xxvii, 263).—The action of one molecule of zinc-methyl upon two molecules of acetyl chloride may be represented by the following equations:—



$$CO\left\{\begin{matrix}Cl\\CH_3\end{matrix}\right. + Zn(CH_3)_2 = CH_3.C\left\{\begin{matrix}Cl\\OZnCH_3\\CH_3\end{matrix}\right.$$

$$CH_3.C\left\{\begin{matrix}Cl\\OZnCH_3\\CH_3\end{matrix}\right. + CO\left\{\begin{matrix}Cl\\CH_3\end{matrix}\right. = 2\left\{\begin{matrix}CH_3\\CO\\CH_3\end{matrix}\right. + ZnCl_2.$$

When the zinc-methyl and acetyl chloride are in the proportion of 2 to 1, trimethylcarbinol is formed, and the quantity produced remains the same when the proportion of zinc-methyl is reduced to one-fourth.

The author has prepared synthetically two representatives of tertiary alcohols containing three different radicles, viz., methylethylpropylcarbinol and methylethylisopropylcarbinol. They are obtained by the action of, first, zinc-methyl, and afterwards zinc-ethyl upon butyril chloride and isobutyryl chloride.

By the action of zinc-ethyl and zinc-methyl upon acetone, mesityl oxide, $C_6H_{10}O$, has been obtained. Its formation is explained by the following equations:—

$$2C_3H_6O + Zn(CH_3)_2 = C_6H_{10}O + 2(CH_4) + ZnO$$
$$2C_3H_6O + Zn(C_2H_5)_2 = C_6H_{10}O + 2(C_2H_6) + ZnO$$

A body, homologous with mesityl oxide, of the formula, $C_9H_{14}O$, has been prepared by the action of propionyl chloride upon zinc-methyl; it is a colourless liquid, insoluble in water, and boiling at 167—168°.

In the action of zinc-ethyl upon butyryl chloride, a liquid of the formula, $C_{10}H_{18}O$ is obtained as a secondary product. It has a peculiar odour, is insoluble in water, and distils at 189—191°.

The formation of dimethylisobutylcarbinol is often accompanied by that of a secondary product of the formula, $C_{10}H_{22}O$. Its formation may be explained by the equation:—

$$2C_6H_{12}O - H_2O = C_{12}H_{22}O.$$

H. H. B. S.

Electrolysis of Aqueous Solutions of Formic Acid. By N BUNGE (*Chem. Centr.*, 1876, 819).—At the negative pole hydrogen was formed; at the positive pole, carbon dioxide, sometimes accompanied by oxygen. The gases were in the proportion of 2 : 2 : 1. The more the conditions of the experiment favour oxidation processes, the greater is the amount of CO_2. The author believes that CHO_2 is first liberated at the + pole, and that this is decomposed by H_2O into CH_2O_2, and free O, which oxidises the electrolytes to CO_2 and H_2O.

M. M. P. M.

Orthothioformic Ethers. By S. GABRIEL (*Deut. Chem. Ges. Ber.*, x, 185).—An aqueous solution of sodium phenylmercaptide, heated with chloroform, yields *phenyl orthothioformate*, $CH(C_6H_5S)_3$. This substance crystallises in short white prisms, which melt at 39·5°, and dissolve in ether, benzene, nitrobenzene, glacial acetic acid, and carbon bisulphide. It is decomposed by fuming hydrochloric acid at 100° in sealed tubes, yielding phenyl mercaptan and formic acid:—

$$CH(SC_6H_5)_3 + 2H_2O = CH_2O_2 + 3C_6H_5(SH).$$

By oxidation with chromic or nitric acid, or with bromine, it yields phenyl disulphide, $(C_6H_5S)_2$, melting at 61°.

Similarly, the corresponding ethyl-ether is readily obtained by heating sodium mercaptide with excess of chloroform.

Ethyl orthothioformate, $CH(C_2H_5S)_3$, forms a mobile, pale-yellow liquid, having a persistent repulsive odour of garlic. It is partially decomposed by distillation. Fuming hydrochloric acid resolves it into ethyl mercaptan and formic acid.

J. R.

β-Amidopropionic and β-Guanidopropionic Acid. By E. MULDER (*Deut. Chem. Ges. Ber.*, ix, 1902—1906).—β-Amidopropionic acid is prepared by converting glycerin into glyceric acid, and this into β-iodopropionic acid, and then into β-amidopropionic acid.

Glyceric acid is best prepared by mixing 50 grams of glycerin (commercial) with 50 grams of water in a large glass tube, placing this in a cellar, and adding, by means of a funnel reaching to the bottom, 50 grams of fuming nitric acid. After 3—4 days the contents of three such tubes are slowly evaporated on the water-bath down to about 270 grams, and the syrupy mass thus obtained is preserved in a flask allowing the escape of the gas, which is slowly given off. 1,620 grams of the syrupy mass are next mixed with 11 litres of water in a tinned copper vessel, and 2,400 grams of white lead are gradually added, and the mixture left to stand for a day. The vessel is then warmed, with constant stirring, to 61—65°, and kept at this temperature for two hours. The liquid is decanted and allowed to deposit crystals, the mother-liquor added to the solid mass, the water lost by evaporation replaced, and the operation repeated two or three times. The lead glycerate thus obtained is almost colourless, and for ordinary purposes need not be recrystallised.

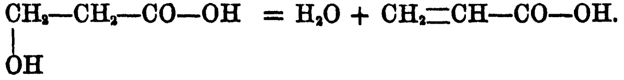
β-Iodopropionic acid. The lead glycerate is decomposed by sulphuretted hydrogen in four flasks, containing 25 grams each, and the filtrate is evaporated down to 100 grams. 150 grams of the glyceric acid and 203 grams of iodine are placed in a litre flask, and 26 grams of a solution of phosphorus in carbon disulphide added through a funnel. The carbon disulphide is expelled by the heat produced by the union of the iodine and phosphorus, and the glyceric acid acts on the phosphorus iodide, which gradually disappears, while a stream of hydriodic acid gas escapes. The whole is converted on cooling into a nearly colourless cake of β-iodopropionic acid. This is placed in a dish with a little water, and left for a few days, when the whole mass becomes converted into tolerably large crystals, which only require washing with water to be fitted for the next step.

β-Amidopropionic acid. β-Iodopropionic acid is treated with strong ammonia at the ordinary temperature—one part of acid to tweuty of ammonia—and the liquid left to itself for some weeks. It is then evaporated with litharge, the residue is extracted with water, and the filtrate, after addition of sulphuretted hydrogen, evaporated on the water-bath. When placed in a desiccator, the liquid becomes a solid, which, after pressing between filter-paper, is dissolved in a little water, and submitted to fractional precipitation with alcohol. The β-amidopropionic acid thus prepared melts at 180°, but after crystallisation from water without addition of alcohol, its melting point is 190°. This acid is very soluble in water, insoluble in alcohol; it is slightly hygroscopic, and possesses but feebly acid properties. Decomposition ensues on heating, in accordance with the equation—

$$NH_2—CH_2—CH_2—CO—OH = NH_3 + CH_2{=}CH—CO—OH.$$

β-Amidopropionic acid behaves analogously to β-iodopropionic and hydracrylic acid :—

$$CH_2I—CH_2—CO—OH = IH + CH_2{=}CH—CO—OH$$



$$\underset{\textstyle OH}{\underset{|}{CH_2}}—CH_2—CO—OH = H_2O + CH_2{=}CH—CO—OH.$$

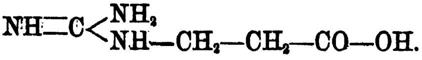
Kaysser has shown that ethylene-lactic acid is identical with hydracrylic acid. There is, therefore, only one compound of the formula,—

$$NH_2—CH_2—CH_2—CO—OH,$$

i.e., β-amidopropionic acid, derived from β-iodopropionic acid, and there is only one of the latter, viz.,—

$$CH_2I—CH_2—CO—OH.$$

As there is only one β-amidopropionic acid, only one β-guanidopropionic acid can exist:—



$$NH{=}C{<}\begin{matrix}NH_2\\ NH{-}CH_2{-}CH_2{-}CO{-}OH.\end{matrix}$$

Correction.—In his communication (*Berichte*, viii, 1293), the author did not intend to assert with certainty that allantoic acid is the decomposition-product of uroxanic acid. However, the formation of urea and glyoxal-urea does not exclude that of allantoic or some isomeric acid. G. T. A.

Action of Alcoholic Potash on Monobromisobutyric Acid.

By CARL HELL and A. WALDBAUER (*Deut. Chem. Ges. Ber.*, x, 448—451).—Monobromisobutyric acid, obtained by heating to 140° in sealed tubes molecular proportions of bromine and isobutyric acid boiling at 154—155°, is a white, nearly inodorous, crystalline mass, melting at 48°. By slow evaporation of its ethereal solution, it may be obtained in large tabular crystals. It boils at 198—200°, with slight decomposition. Sp. gr. at 60° = 1·5225; at 100° = 1·500, water at the same temperatures being 1. It dissolves in alcohol, ether, carbon bisulphide, chloroform, benzene, &c. When boiled with water, it is slowly but completely resolved into hydrobromic acid, and oxyisobutyric acid melting at 80°. It is completely decomposed by aqueous silver nitrate, slowly in the cold, and more rapidly when heated.

The *ethylic ether* of monobromisobutyric acid, obtained by passing hydrogen chloride into an alcoholic solution of the acid, boils at 160° (corr.).

Monobromisobutyric acid in alcoholic solution is decomposed by alcoholic potash, yielding potassium bromide, and the potassium salt of the following acid.

Ethoxyisobutyric acid, $\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}{>}C(OC_2H_5).COOH$, is a colourless liquid, of penetrating ethereal odour, and pungent burning taste, soluble in alcohol and ether, and sparingly in water. Sp. gr. at 0° = 1·0211; at 16° = 1·0101, water at the same temperatures being 1. It forms easily soluble and crystallisable salts.

The *silver salt*, $C_6H_{11}O_3Ag$, crystallises from hot water in fine white laminæ, which in the moist state quickly turn brown in the light.

The *lead salt*, $(C_6H_{11}O_3)_2Pb + H_2O$, crystallises from water, in fine white translucent prisms.

The *barium salt*, $(C_6H_{11}O_3)_2Ba + H_2O$, forms thick transparent prisms.

The *zinc salt*, $(C_6H_{11}O_3)_2Zn$, when freshly prepared, crystallises from hot water in fine pearly laminæ, which gradually lose water when dried by heat, or over sulphuric acid, and yield an insoluble basic salt.

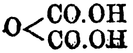
The *copper salt* forms fine green laminæ; the *sodium salt* a granular crystalline mass; both easily soluble in water and alcohol.

J. R.

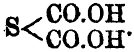
Conversion of Ricinoleic Acid into Stearic Acid. By A. CLAUS (*Deut. Chem. Ges. Ber.*, ix, 1916—1918).—The author prepares pure ricinoleic acid by fractional precipitation of crude ricinoleic acid soap with calcium chloride. The first third of the precipitate is rejected, and the remainder, crystallised from alcohol, consists of pure calcium ricinoleate. When ricinoleic acid is shaken up with water, so as to form an emulsion, and phosphorus and iodine are gradually added to this on the water-bath, a yellowish or yellowish-brown oil, heavier than water, is obtained, the formula of which is $C_{18}H_{33}IO_2$. For this body the author proposes the name of *iodostearidenic acid*. This acid takes up two atoms of bromine, and forms iododibromostearic acid, $C_{18}H_{33}Br_2IO_2$.

Stearic acid is easily prepared from iodostearidenic acid by heating it with zinc and hydrochloric acid. G. T. A.

The Sulpho-dicarbonic Acids. By HERMANN WELDE (*J. pr. Chem.* [2], xv, 43—62).—Some years ago Victor Meyer drew attention to the possibility of the existence of dicarbonic acids in which sulphur as well as oxygen forms the copula for the carboxyl groups:



$$O<{CO.OH \atop CO.OH}$$

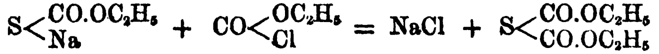


$$S<{CO.OH \atop CO.OH}\cdot$$

He also considered it possible that nitrogen and carbon copulæ might be introduced, and tri- and tetra-carbonic acids formed. Meyer thought the existence of such acids in the free state improbable, but that their ethers might be capable of existence. By the action of ethyl-chlorocarbonate on alcoholic sodium sulphide, Meyer obtained ethyl thiodicarbonate:—

$$Na_2S + 2CO(OC_2H_5)Cl = S(CO.OC_2H_5)_2 + 2NaCl.$$

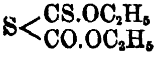
The reaction takes place probably in two stages, sodium ethylmonosulphocarbonate being formed, and decomposed by a second molecule of ethyl chlorcarbonate:



$$S<{CO.OC_2H_5 \atop Na} + CO<{OC_2H_5 \atop Cl} = NaCl + S<{CO.OC_2H_5 \atop CO.OC_2H_5}$$

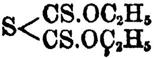
Sodium ethylmono-thiocarbonate. Ethylthiodicarbonate.

Now on replacing oxygen by sulphur in the above ethylthiodicarbonate, a system of new bodies makes its appearance:



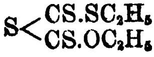
$$S<{CS.OC_2H_5 \atop CO.OC_2H_5}$$

(1.)



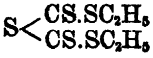
$$S<{CS.OC_2H_5 \atop CS.OC_2H_5}$$

(2.)



$$S<{CS.SC_2H_5 \atop CS.OC_2H_5}$$

(3.)



$$S<{CS.SC_2H_5 \atop CS.SC_2H_5}$$

(4.)

In attempting to get No. 1, the author stumbled unexpectedly upon No. 2.

Ethyl thiodisulphodicarbonate, $S(CS.OC_2H_5)_2$. Prepared by dropping ethyl chlorocarbonate into an alcoholic solution of potassium xanthate with repeated shaking. The mixture was left for several days in a well-closed flask, and from time to time vigorously shaken. The oil which settled down was separated from the precipitate by filtration, and washed with much cold water, under which it soon formed a crystalline mass insoluble in water, soluble in ether, and very soluble in alcohol. Repeated crystallisation from alcohol yielded beautiful golden needles of the new compound. Melting point 55°. The equation realised was therefore:

$$3\mathrm{CS(OC_2H_5)(SK)} + 2\mathrm{CO(OC_2H_5)Cl} = 2\mathrm{S(CS.OC_2H_5)_2} + 2\mathrm{KCl} + \mathrm{CO(OC_2H_5)OK},$$

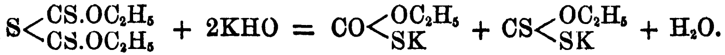
and not, as expected—

$$\mathrm{CO(OC_2H_5)Cl} + \mathrm{CS(OC_2H_5)SK} = \mathrm{S(CS.OC_2H_5)CO.OC_2H_5)} + \mathrm{KCl}.$$

The new ether was now treated in different ways for the purpose of throwing light upon its constitution.

Behaviour with potash. Ethyl thiodisulphodicarbonate dissolved in alcohol and treated with a concentrated solution of alcoholic potash, yielded a mixture of Bender's salt, $\mathrm{CO(OC_2H_5)SK}$, less soluble portion, and potassium xanthate, $\mathrm{CS(OC_2H_5)SK}$, more soluble portion. These were separated by recrystallisation.

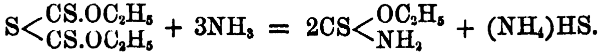
The action of potassium hydrate on the above is represented as follows:—



$$\mathrm{S}{<}\begin{matrix}\mathrm{CS.OC_2H_5}\\\mathrm{CS.OC_2H_5}\end{matrix} + 2\mathrm{KHO} = \mathrm{CO}{<}\begin{matrix}\mathrm{OC_2H_5}\\\mathrm{SK}\end{matrix} + \mathrm{CS}{<}\begin{matrix}\mathrm{OC_2H_5}\\\mathrm{SK}\end{matrix} + \mathrm{H_2O}.$$

Ethylthiodisulphodicarbonate. Bender's salt. Potassium xanthate.

Behaviour with ammonia. The ether was now dissolved in alcohol and mixed with excess of alcoholic ammonia, the mixture being allowed to stand for a long time. The solution evaporated on the water-bath leaves large colourless crystals consisting of xanthamide, the mother-liquors containing ammonium sulphide:

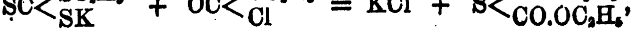


$$\mathrm{S}{<}\begin{matrix}\mathrm{CS.OC_2H_5}\\\mathrm{CS.OC_2H_5}\end{matrix} + 3\mathrm{NH_3} = 2\mathrm{CS}{<}\begin{matrix}\mathrm{OC_2H_5}\\\mathrm{NH_2}\end{matrix} + \mathrm{(NH_4)HS}.$$

Xanthamide.

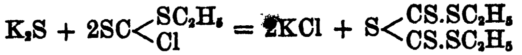
The above reactions with potash and ammonia amply prove the formula $\mathrm{S(CS.OC_2H_5)_2}$ to be the correct one for this new ether, which is therefore ethylthiodisulphodicarbonate.

When ethylchlorocarbonate was allowed to act on potassium xanthate, equal quantities being taken, a yellow oil was obtained after separation with cold water. This could not be crystallised, and analysis gave unsatisfactory results. The author had hoped to obtain the ethers $\mathrm{S(CS.SC_2H_5)(CO.OC_2H_5)}$ and $\mathrm{S(CS.SC_2H_5)_2}$, the former by the action of ethyl chlorcarbonate on potassium-ethyl trisulphocarbonate:—

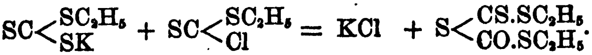


$$\mathrm{SC}{<}\begin{matrix}\mathrm{SC_2H_5}\\\mathrm{SK}\end{matrix} + \mathrm{OC}{<}\begin{matrix}\mathrm{OC_2H_5}\\\mathrm{Cl}\end{matrix} = \mathrm{KCl} + \mathrm{S}{<}\begin{matrix}\mathrm{CS.SC_2H_5}\\\mathrm{CO.OC_2H_5}\end{matrix},$$

the latter by the two following methods:—



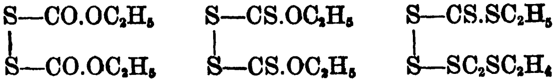
$$K_2S + 2SC<\substack{SC_2H_5\\Cl} = 2KCl + S<\substack{CS.SC_2H_5\\CS.SC_2H_5}$$



$$SC<\substack{SC_2H_5\\SK} + SC<\substack{SC_2H_5\\Cl} = KCl + S<\substack{CS.SC_2H_5\\CO.SC_2H_5}.$$

The chloride $SC<\substack{SC_2H_5\\Cl}$ could not, however, be prepared, though many efforts were made, nor could the potassium-ethyl trisulphocarbonate be obtained pure.

In another class of bodies allied to the preceding, two sulphur atoms are bound together, the two remaining affinities being saturated by ethylated carboxyl groups. In the latter a part or the whole of the oxygen can be replaced by sulphur:



$$\begin{array}{lll} S—CO.OC_2H_5 & S—CS.OC_2H_5 & S—CS.SC_2H_5 \\ | & | & | \\ S—CO.OC_2H_5 & S—CS.OC_2H_5 & S—SC_2SC_2H_4 \end{array}$$

(1.) (2.) (3.)

No. 1. Prepared by the action of alcoholic iodine solution on Bender's salt (Debus):

$$2CO(OC_2H_5)SK + I_2 = 2KI + S_2(CO.OC_2H_5)_2.$$

No. 2. By treating potassium xanthate with alcoholic iodine solution (Desains):

$$2CS(OC_2H_5)SK + I_2 = S_2(CS.OC_2H_5)_2 + 2KI.$$

Ethyl dithiodisulphocarbonate.

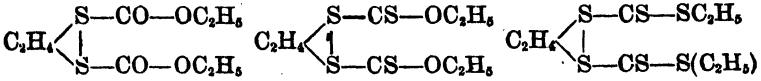
No. 3. By treating ethyl-potassium trisulphocarbonate with alcoholic iodine solution (Salomon):

$$2CS(SC_2H_5)SK + I_2 = S_2(CS.SC_2H_5)_2 + 2KI.$$

Ethyldithiotetrasulphocarbonate.

Regarding the constitution of the above, the author was led to imagine it possible that compounds should exist in which the two sulphur affinities should, instead of saturating one another, be knit to and centred upon a diatomic radical, like ethene, for example:

I. II. III.



$$C_2H_4<\substack{S—CO—OC_2H_5\\ | \\ S—CO—OC_2H_5} \quad C_2H_4<\substack{S—CS—OC_2H_5\\ | \\ S—CS—OC_2H_5} \quad C_2H_4<\substack{S—CS—SC_2H_5\\ | \\ S—CS—S(C_2H_5)}$$

Ethyl dithioethenecarbonate. Ethyl dithioethenedisulphocarbonate. Ethyl dithioethenetetrasulphocarbonate.

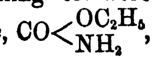
These expectations were realised, and the following are briefly the methods of preparation:—

I. *Ethyl dithio-ethenecarbonate.* Obtained by the action of ethene bromide on "Bender's salt:"

$$2CO(OC_2H_5)SK + C_2H_4Br_2 = (C_2H_4)S_2(CO.OC_2H_5)_2 + 2KBr.$$

Thus a weighed quantity of "Bender's salt" (obtained by passing carbon oxysulphide, COS, into alcoholic potash) was stirred with alcohol to a paste, and warmed for several hours with the calculated quantity of ethene bromide. A thick white precipitate was obtained which was collected on a filter, and the thick oil draining off was separated and well washed with water. It was finally dried in the exsiccator over phosphorus pentoxide. This ether is a thick clear yellow oil, with an unpleasant odour. It is insoluble in water, but soluble in alcohol and ether. The oil was decomposed by distillation, with liberation of mercaptan. Potash has the following action upon it:—

$$(C_2H_4)S_2(CO.OC_2H_5)_2 + 2KHO = \underset{\text{Potassium ethyl carbonate.}}{2CO(OC_2H_5)OK} + \underset{\text{Ethene sulphydrate.}}{C_2H_4(SH)_2}.$$

Ammonia in alcoholic solution and excess was now shaken with the ether, and the whole left for several days, and then evaporated on the water-bath. Beautiful white crystals and a bad smelling oil were obtained. The former body was proved to be *urethane*,  $CO<\begin{matrix}OC_2H_5\\NH_2\end{matrix}$, the latter (oil), *ethene sulphydrate*, $C_2H_4(SH)_2$. The reaction is, therefore, as follows:—

$$(C_2H_4)S_2(CO.OC_2H_5)_2 + 2NH_2 = 2CO(OC_2H_5)NH_2) + C_2H_4(SH)_2.$$

II. *Ethyl dithioethenedisulphocarbonate.* Obtained by the action of ethene bromide on potassium xanthate in alcoholic solution. The reaction begins at once, and with a little warming is soon complete. A dense precipitate is obtained from which an oil is separated by filtration and much washing. This oil soon solidifies to a crystalline mass. This is dried between blotting-paper, and recrystallised from ether. By quickly evaporating, the body is obtained in long white needles; on slowly crystallising, rhombic tables are obtained. The crystals are insoluble in water, but soluble in alcohol and ether. Melting point = 42°. The reaction by which the body was obtained is expressed as follows:—

$$\underset{\text{Potassium xanthate.}}{2CS(OC_2H_5)SK} + C_2H_4Br_2 = \underset{\text{Ethyl dithioethenedisulphocarbonate.}}{(C_2H_4)S_2(CS.OC_2H_5)_2} + 2KBr$$

On treating an ethereal solution of this body with a concentrated solution of potash in absolute alcohol, the following reaction occurs:—

$$S_2(CS.OC_2H_5)_2 + 2KHO = \underset{\text{Potassium xanthate.}}{2CS(OC_2H_5)SK} + C_2H_4O + H_2O$$

On treating it with excess of ammonia, no action appeared at first to take place. The mixture was now carefully evaporated on the water-bath, whereby an oily residue and a beautifully crystalline body were obtained. The latter turned out to be xanthamide. The reaction is thus expressed—

$$(C_2H_4)S_2(CS.OC_2H_5)_2 + 2NH_3 = \underset{\text{Xanthamide.}}{2CS(OC_2H_5)(NH_2)} + C_2H_4{<}\genfrac{}{}{0pt}{}{SH}{SH}$$

III. *Ethyl dithioethenetetrasulphocarbonate.* By the action of ethenebromide on an alcoholic solution of ethyl-potassium trisulphocarbonate, potassium bromide and a yellow oil were obtained. Analyses of the latter led to the conclusion that this was no other than the desired ether above named. No numbers are, however, given, since completely pure potassium ethyl trisulphocarbonate could not be obtained. The oil mentioned had an odour so penetrating and repulsive that this, added to the other above-named difficulty, has for the present deterred the author from further experiment.

The anticipated reaction was:—

$$2CS(SC_2H_5)SK + C_2H_4Br_2 = \underset{\text{Ethyl dithioethenetetrasulphocarbonate.}}{(C_2H_4)S_2(CS.SC_2H_5)_2} + 2KBr$$

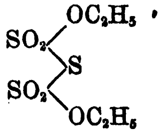
Glancing retrospectively at the various reactions dealt with, the author notices several interesting analogies and parallelisms. Potassium xanthate is converted by alcoholic iodine into ethyl dithiodisulphocarbonate, and in a similar manner sodium thiosulphate is converted into sodium tetrathionate:—

$$\underset{\text{Potassium xanthate.}}{2CS(OC_2H_5)SK} + I_2 = S_2(CS.OC_2H_5)_2 + 2KI$$

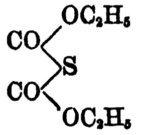
$$\underset{\text{Sodium thiosulphate.}}{2\left(SO_2{<}\genfrac{}{}{0pt}{}{ONa}{SNa}\right)} + I_2 = \underset{\text{Sodium tetrathionate.}}{S_2(SO_2.ONa)_2} + 2NaI.$$

In like manner ethyl thiodisulphocarbonate, $S(CS.OC_2H_5)_2$, with its method of preparation is analogous to sodium trithionate $S(SO_2.ONa)_2$ with its method of preparation.

It has been pointed out by Dr. Keil how, if the analogue of ethyl chlorcarbonate $\left(CO{<}\genfrac{}{}{0pt}{}{OC_2H_5}{Cl}\right)$, viz., the sulpho-compound, $SO_2{<}\genfrac{}{}{0pt}{}{OC_2H_5}{Cl}$, were prepared, other sulphuryl compounds could be constructed. Thus by the action of $SO_2{<}\genfrac{}{}{0pt}{}{OC_2H_5}{Cl}$ on an alcoholic solution of Na_2S, the ethyl trithionate should be obtained, just as Victor Meyer obtained the ethyl thiodicarbonate.



Ethyl trithionate.

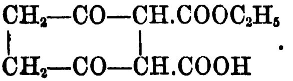


Ethyl thiodicarbonate.

W. S.

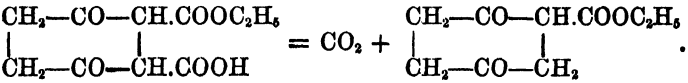
Action of Alkali-metals on Ethyl Succinate. By F. HERMANN (*Deut. Chem. Ges. Ber.*, x, 107—112).—The author stated in a previous paper that the product of this action is a body which he proposes to call *di-ethyl succinylsuccinate.* The reactions of this body have now been further examined. In alkaline solution it undergoes a kind of decomposition, which varies to some extent, according as it takes place in the absence or presence of air.

I. *Decomposition of Diethyl Succinylsuccinate in Alkaline Solution in the Absence of Air.*—1. When the yellow alkaline solution is left for two hours, the undecomposed ether then precipitated by carbon dioxide, and the filtered liquid acidified with acetic acid, there is thrown down a crystalline greenish-white powder, which is sparingly soluble in cold alcohol, ether, and cold water. Neutral solutions of this body are coloured deep violet by ferric chloride. It melts at 98°, evolving carbon dioxide, to a pale yellow liquid, which does not solidify, and is readily decomposed by boiling water, with copious evolution of carbon dioxide. According to analysis the substance is *monethyl succinylsuccinate*, having the formula—



$$\begin{array}{l}CH_2{-}CO{-}CH.COOC_2H_5\\ |\qquad\quad\ \ |\\ CH_2{-}CO{-}CH.COOH\end{array}.$$

This formula is supported by the facts that the substance yields alcohol when heated with potash, and that it gives off at 100° a quantity of carbon dioxide, agreeing with the following equation, thus yielding *ethyl succinylproprionate*:—



$$\begin{array}{l}CH_2{-}CO{-}CH.COOC_2H_5\\ |\qquad\quad\ \ |\\ CH_2{-}CO{-}CH.COOH\end{array} = CO_2 + \begin{array}{l}CH_2{-}CO{-}CH.COOC_2H_5\\ |\qquad\quad\ \ |\\ CH_2{-}CO{-}CH_2\end{array}.$$

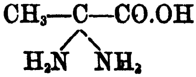
The last product, which has been analysed by the author, is an oily liquid of intensely bitter taste and faint odour, dissolving easily in alcohol and ether, and sparingly in cold water. Its solutions are coloured a pure violet by ferric chloride.

2. In the liquid filtered from monethyl succinylsuccinate, dilute sulphuric acid produces a yellowish-white, crystalline precipitate of acid reaction, sparingly soluble in cold water, and more freely in alcohol and ether. The solutions are coloured violet by ferric chloride. This substance is readily decomposed by boiling water, evolving carbon dioxide. It is regarded by the author as *succinylsuccinic acid.*

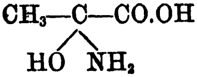
3. The liquid from which the preceding substances have been separated contains yet another decomposition-product, which has not been isolated.

II. *Decomposition of Diethyl Succinylsuccinate in Alkaline Solution in presence of Air.*—In presence of air, the decomposition described above is accompanied by absorption of oxygen, in consequence of which there is formed, besides the foregoing decomposition-products, an acid which crystallises from boiling water in pale yellow, hair-like needles. This body dissolves very easily in alcohol, ether, and boiling water, the solutions exhibiting a greenish fluorescence, and giving a deep blue colour with ferric chloride. When cautiously fused with potash and afterwards acidified with sulphuric acid, it evolves carbon dioxide and yields hydroquinone. From these reactions, and the numbers obtained by analysis, the author concludes that the substance is *hydroquinone-dicarbonic acid*, $C_6O_2H_4(COOH)_2$. J. R.

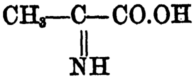
The Action of Ammonia and Amido-derivatives on Pyroracemic Acid. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, x, 362—369).—I. *Action of Alcoholic Ammonia.*—If the constitution of pyroracemic acid be expressed by $CH_3—CO—CO.OH$, then theoretically, the following compounds will be obtainable:—

(1.) 

$CH_3—\underset{H_2N\ \ NH_2}{C}—CO.OH$

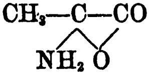
(2.) 

$CH_3—\underset{HO\ \ NH_2}{C}—CO.OH$

(3.) 

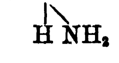
$CH_3—\underset{\overset{\|}{NH}}{C}—CO.OH$

No 3 is obtained from No. 2 by abstraction of water, and this can take place in another way, so that a compound may be formed of the following constitution:—

(4.) 

$CH_3—\underset{NH_2\ \ O}{C}—CO$

The foregoing become more complicated on consideration of the strong tendency of pyroracemic acid to split up, with evolution of carbonic acid. The simplest body that could be formed in this way would be the aldehyde-ammonia:—

(5.) 

$CH_3—\underset{H\ \ NH_2}{C}—OH$

Gaseous ammonia acts so strongly on pyroracemic acid, that a liberation of carbon dioxide takes place, and the whole becomes warm. The product is an oil, which, after standing some time, acquires an acid reaction, dissolves in alcohol, and is separated out by ether. Only in one case was a very small quantity of a white precipitate obtained by this method of treatment. It was treated with calcium hydrate, in order to liberate ammonia. The lime salt produced consisted of a mixture of modified pyroracemic acid and calcium acetate, which could be separated by successive treatment with water and alcohol. Concentrated aqueous ammonia acts less powerfully on pyroracemic acid; on warming the action becomes more energetic. But by using concentrated alcoholic ammonia, a vigorous action is set up, with development of considerable heat. The acid should be allowed to flow cautiously into the alcoholic ammonia, too great development of heat being checked by cooling. A white precipitate is formed, and a body remains dissolved in the solution. The solution was at once separated from the precipitate for fear of further changes in the hot solution.

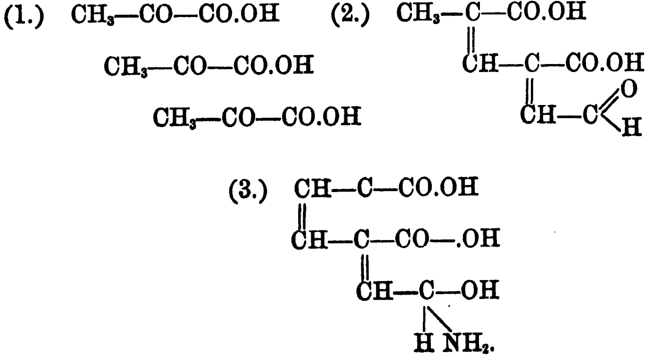
The precipitate was washed with alcohol, and dissolved in cold water. The alcoholic and aqueous solutions were now set aside to evaporate. The aqueous solution after some time separated out a crystalline body, which was drained on a tile, washed with cold water, redissolved, and again left to crystallise. Finally, a white chalky powder was obtained, which on warming with sodium hydrate, gave off ammonia. Analysis gave numbers corresponding with the formula, $n(C_4H_6NO_2)$. As already mentioned, the body shows an acid reaction. It is soluble in ammonia, and is reprecipitated on addition of hydrochloric acid, as a white powder, almost entirely insoluble in cold water, with difficulty in boiling water. In the pure state, on boiling with caustic soda, this body evolves ammonia. It is an extremely stable acid. To obtain it easily and quickly, the aqueous solution of the precipitate produced by alcoholic ammonia, was evaporated on the water-bath, when ammonia and carbonic acid were evolved, and the solution changed from alkaline to acid, becoming yellow coloured during the process. On addition of hydrochloric acid, a flesh-coloured precipitate separated, consisting of the impure acid in question. This was obtained pure and colourless by repeated washing with water, and reprecipitation from ammoniacal solution by hydrochloric acid. When heated to a high temperature, it partly sublimes, and partly chars. The acid was dried and analysed, and gave numbers corresponding with the formula, $C_8H_9NO_4$, which formula stands in close relationship to that of the last-named body, $C_8H_9NO_4 + NH_3 = 2(C_4H_6NO_2)$, which is therefore the acid ammonium salt. The acid easily dissolves in cold baryta-water. By passing carbonic acid through this solution, boiling, filtering, and concentrating, a barium salt was obtained, insoluble in cold, slightly soluble in hot water.

The barium salt contains one molecule of water, which it obstinately retains, even at a temperature of 160°. Its formula is $C_8H_7BaNO_4 + 3H_2O$. The *silver salt* is $C_8H_7NAg_2O_4 + H_2O$.

The new acid is named *uvitonic acid.* Its manner of formation may be expressed by the following scheme:—

Properly speaking the body in the free state is an *anhydride*, the acid not appearing to exist in the free state.

Pyroracemic acid (3 mols.).


(1.) $CH_3—CO—CO.OH$

$CH_3—CO—CO.OH$

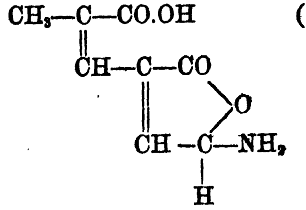
$CH_3—CO—CO.OH$

(2.)

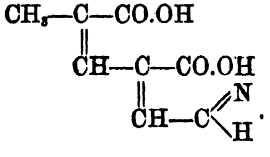
(3.)

Only two assumptions in relation to the formation of the anhydride can be made :—

(3*a*.)



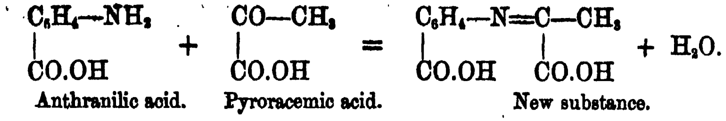
(3*b*.)



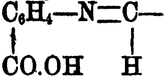
The formula 3*a* is held to be the most suitable expression for the properties of the body. The alcoholic ammoniacal solution, on evaporation and treatment with calcium-hydrate, suffered a decomposition, whereby calcium pyroracemate and acetate were formed. It was satisfactorily proved that this solution contained an amido-group. It is proposed next to treat pyroracemic acid with aniline, in the same way as has been done with ammonia, in the hope of obtaining more easily the normal bodies.

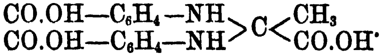
II. *Action of Anthranilic Acid on Pyroracemic Acid.*—On warming anthranilic acid till it fuses, and then adding it to pyroracemic acid, a vigorous reaction sets in, accompanied by rise of temperature and evolution of carbon dioxide. The whole requires cooling, to prevent the action from becoming too violent. The chief product is a yellow substance, nearly insoluble in water, and but slightly in alcohol and ether. To purify it, the mass is treated repeatedly with boiling water. The residual mass on the filter is now dissolved in the smallest possible amount of ammonia, the solution placed in a tap-funnel, diluted, and mixed, first with hydrochloric acid, and then with ether. The acid is separated out by the former, and collects between the aqueous and ethereal layers. The substance is washed at first with small quantities of water, and finally with ether, till quite colourless. When dry, it forms a loose yellow powder.

As already mentioned, a large quantity of carbon dioxide escapes during the preparation of this body. On heating to 135° it continues to lose carbon dioxide, and exhibits the behaviour both of pyroracemic acid and of anthranilic acid, which itself at high temperatures decomposes into carbon dioxide and aniline. Heated between watch-glasses on the sand-bath, the substance melts, after copious evolution of carbon dioxide, to a dark-coloured liquid, which sublimes in small oily drops, quickly solidifying in the crystalline state. The residual substance now dissolves, both in ammonia and sulphuric acid. The sublimate mentioned is of a basic nature, dissolving in sulphuric acid, and being precipitated from this solution by ammonia as a white precipitate. No examination of this body has yet been made. It is evidently a mixture, and a good method of separation has not yet been hit upon. It is, however, considered almost certain that in the formation of the body, a molecule of pyroracemic acid has reacted upon one of anthranilic acid, a substance of the following formula being produced :—



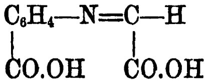
$$\begin{array}{l}C_6H_4\text{—}NH_2\\ |\\ CO.OH\end{array} + \begin{array}{l}CO\text{—}CH_3\\ |\\ CO.OH\end{array} = \begin{array}{lll}C_6H_4\text{—}N&=&C\text{—}CH_3\\ |&&|\\ CO.OH&&CO.OH\end{array} + H_2O.$$

By loss of CO_2 from the molecule of pyroracemic acid, the body,  $\begin{array}{lll}C_6H_4\text{—}N&=&C\text{—}CH_3\\ |&&|\\ CO.OH&&H\end{array}$ might arise. The excess of carbon found by analysis, testifies to the probability of the formation of this body. The nitrogen estimations also permit the assumption of the formation of a compound of the following formula:—

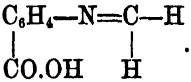


$$\begin{array}{l}CO.OH\text{—}C_6H_4\text{—}NH\\ CO.OH\text{—}C_6H_4\text{—}NH\end{array}\!\!>C<\!\!\begin{array}{l}CH_3\\ CO.OH\end{array}\cdot$$

An extremely interesting and remarkable reaction is further observed of this body. When suspended in water and exposed to sunlight, it quickly becomes of a deep blue colour. At present it is impossible to say which of the substances in the mixture it is that is so peculiarly acted upon. The author hopes to extend the reaction to glyoxylic acid, whereby he expects to obtain the bodies:—

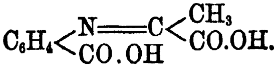
(1.) 

$$\begin{array}{lll}C_6H_4\text{—}N&=&C\text{—}H\\ |&&|\\ CO.OH&&CO.OH\end{array}$$

(2.) 

$$\begin{array}{lll}C_6H_4\text{—}N&=&C\text{—}H\\ |&&|\\ CO.OH&&H\end{array}.$$

The empirical formula of the second body differs from that of indigo only by containing one molecule of water more. The body was dried at 135°, and analysed; the barium salt was also prepared and analysed. On drying the latter at 130°, it became blue on the surface. The results obtained led to the formula—



$$C_6H_4<\!\!\begin{array}{l}N=\!=\!=C\\ CO.OH\end{array}\!\!<\!\!\begin{array}{l}CH_3\\ CO.OH.\end{array}$$

W. S.

Tartronamic Acid. By N. Menschutkin (*Bull. Soc. Chim.* [2], xxvii, 261).—Tartronamic acid is obtained by treating sodic dialurate for several hours with boiling water. It crystallises in the form of long, colourless, and transparent prisms; heated to its melting point (160°), it decomposes. In its empirical formula and physical properties, this acid resembles amidomalonic acid, but its reactions show that the two substances are not identical.

Tartronamic acid forms crystallisable salts. A solution of iodine in potassium iodide has no action upon it. The products of its decomposition are glycollic acid, carbonic acid, and ammonia.

H. H. B. S.

Occurrence of an Amide of Glutamic Acid in the young Plants of the Pumpkin. By Ernst Schulze and J. Barbieri (*Deut. Chem. Ges. Ber.*, x, 199—201).—The authors have obtained glutamic acid, $C_5H_9NO_4$, from young pumpkin plants, by boiling with hydrochloric acid an extract of the plants made with equal parts of alcohol and water. The acid appears to exist in the plant in the form of an amide, since it is obtained only after boiling the extract with hydrochloric acid. The yield of the acid amounts to about 1·75 per cent. of the dry substance of the plants. J. R.

Laws of Substitution in Benzene. By E. Nölting (*Chem. Centr.*, 1876, 805).—1. When a neutral, basic, or feebly acid group, such as CH_3, Cl, Br, I, NH_2, OH, is introduced into position 1, and when the substance so obtained is acted upon by Cl, Br, I, HNO_3, or H_2SO_4, para- (1 : 4) derivatives are mainly obtained, accompanied by variable, but always small quantities of ortho- (1 : 2) derivatives. 2. If an acid group, NO, COOH, SO_3H be in position 1, and if this substance be acted upon by the reagents above enumerated, the main products are meta- (1 : 3) derivatives, together with small quantities of ortho- and para-derivatives. The groups, $COOC_2H_5$, COH, $CO.CH_3$, $SO_2.C_6H_5$, appear to behave similarly to the acid groups, COOH and SO_3H; $CH_2.COOH$,$CH_2.CH_2.COOH$, and CH.CH.COOH, on the other hand behave like the neutral group, CH_3; and CN appears to be intermediate between these two sets.

If a third atom or group enter into a di-derivative, C_6H_4AB, the groups A and B both exert an influence upon the entering atom, and the position of this atom is determined according as the influence of A or B predominates. So far as observation has extended, the following generalisations hold good.

If A be represented by the group OH, then this group exercises a predominating influence upon all entering groups, Cl, Br, I, SO_3H, NO_2, independently of the nature of B, which may be Cl, Br, I, NH_2, NO_2, COOH, or SO_3H.

If A be NH_2, then it exerts a predominating influence in the most marked manner when B is other than OH.

If A is other than OH or NH_2, different cases may be distinguished:—

(*a.*) A and B are in the 1 : 4 or 1 : 2 position; their influence is equal.

(*b.*) A and B are in the 1 : 3 position; further substitution proceeds as if 3 were unoccupied.

It follows also that if A and B are in 1 : 4 position, the new group goes into 2, and the next substituted group into 6; if A and B are in 1 : 2, the next group goes into 4, and simultaneously to a less degree into 6. A fourth group forms in that case a 1 : 2 : 4 : 6 derivative from these two.

A 1 : 3 derivative, on further substitution, comports itself as a mono-substitution product. M. M. P. M.

Action of Stannic Chloride on Benzene. By B. Aronheim (*Deut. Chem. Ges. Ber.*, ix, 1898—1899).—The mixed vapours of benzene and stannic chloride were passed through a red-hot tube, when, instead of the anticipated reaction—

$$SnCl_4 + C_6H_6 = HCl + C_6H_5SnCl_3,$$

stannous chloride, diphenyl, and hydrochloric acids were produced:

$$SnCl_4 + 2C_6H_6 = SnCl_2 + (C_6H_5)_2 + 2HCl.$$

This corresponds with the experiments of Smith (see this Journal, 1876, ii, 30). G. T. A.

Disulphocyanobenzene. By S. GABRIEL (*Deut. Chem. Ges. Ber.*, x, 184).—When the lead salt of benzene disulphhydrate (metathioresorcin, melting at 27°) is digested at 100° with an alcoholic solution of cyanogen iodide, lead iodide is deposited and metadisulphocyanobenzene, $C_8H_4N_2S_2$, is formed. The latter product is thrown down on adding water to the alcoholic liquid, and crystallises from hot alcohol in colourless transparent needles which melt at 54°. It dissolves easily in benzene, ether, glacial acetic acid, and carbon bisulphide, sparingly in cold alcohol. It is converted by a mixture of sulphuric and nitric acids into *nitrodisulphocyanobenzene*, a body crystallising from boiling alcohol in short yellow needles, which dissolve in glacial acetic acid and hot nitrobenzene, and melt at 150°. J. R.

Action of Antimonious Chloride upon Azobenzene. By BOGDANOFF (*Chem. Centr.*, 1876, 820).—A black, amorphous, substance, with metallic appearance was obtained. Azophenylene was not produced. M. M. P. M.

Preparation of Monomethylaniline. By A. KERN (*Deut. Chem. Ges. Ber.*, x, 195—199).—The author finds that aniline and methyl iodide when mixed together react in the manner indicated by the equation—

$$3(C_6H_5.NH_2) + 2CH_3I = C_6H_5.N(CH_3)_2 + 2(C_6H_5.NH_2.HI),$$

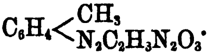
the products being dimethylaniline and aniline hydriodide. The statement found in all text-books, namely, that equivalent proportions of aniline and methyl iodide yield monomethylaniline hydriodide, are therefore, not true. Monomethylaniline is not formed by the reaction of these bodies in any proportions, and it has probably never yet been prepared. J. R.

Azo-compounds of Methazonic Acid. By C. KIMICH (*Deut. Chem. Ges. Ber.*, x, 140—144).—*Azophenyl-methazonic acid.* This compound is precipitated in orange-red flocks on adding a solution of azodibenzene nitrate to an aqueous solution of sodium methazonate. It crystallises from alcohol or ether in fine orange-red needles, which melt with decomposition at 164°. It is nearly insoluble in water, but easily soluble in alcohol, ether, and chloroform. Alkalis dissolve it with deep-red, strong sulphuric acid with yellow colour. The substance dried over sulphuric acid agrees in composition with the formula $C_8H_8N_4O_3$. Its formation is expressed by the equation—

$$C_2H_3NaN_2O_3 + C_6H_5.N_2.NO_3 = NaNO_3 + C_6H_5.N_2.C_2H_3N_2O_3.$$

The aqueous solution of the sodium salt of azophenyl-methazonic acid ($C_8H_6N_4O_3Na_2 + 2H_2O$) gives coloured precipitates with copper, cadmium, zinc, mercury, and silver salts. The barium salt ($C_8H_6N_4O_3Ba + H_2O$) is a purple-red powder.

Azoparatolylmethazonic acid, obtained in the same manner as the preceding substance, forms orange-coloured needles, which melt at 154°, undergoing decomposition. It dissolves sparingly in water, very easily in alcohol and ether. Its composition agrees with the formula



$$C_6H_4<^{CH_3}_{N_2C_2H_3N_2O_3}.$$

J. R.

Chrysoïdin. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, x, 213—218).—The author has examined the dye-stuff known by this name in commerce. Its composition agrees with the formula $C_{12}H_{12}N_4,HCl$, and it forms a platinum double-salt agreeing with the formula $2(C_{12}H_{12}N_4,HCl),PtCl_4$, whence it appears that chrysoïdin is the hydrochloride of diamidazobenzene, a body intermediate between aniline-yellow and phenylene-brown:

Monamidazobenzene, $C_{12}H_9(NH_2)N_2 = C_{12}H_{11}N_3$ (aniline-yellow);
Diamidazobenzene, $C_{12}H_8(NH_2)_2N_2 = C_{12}H_{12}N_4$ (chrysoïdin);
Triamidazobenzene, $C_{12}H_7(NH_2)_3N_2 = C_{12}H_{13}N_5$ (phenylene-brown).

Chrysoïdin is readily decomposed by soda or ammonia, its base being precipitated in pale-yellow flocks, which dissolve sparingly in water and easily in alcohol and ether. The base crystallises with difficulty. It melts at 110°. With nitric acid it forms a red crystallisable salt, closely resembling chrysoïdin.

The author finds that the salt just mentioned (diamidoazobenzene nitrate) is formed when phenylene-diamine is added to a solution of diazobenzene nitrate, the following reaction then taking place:—

$$C_6H_4N_2.HNO_3 + C_6H_8N_2 = C_{12}H_{12}N_4.HNO_3.$$

The nitrate thus formed gives, on addition of ammonia, a precipitate which forms with hydrochloric acid a salt identical with commercial chrysoïdin.

In the same manner a whole series of colouring matters analogous to chrysoïdin may be obtained. Thus, instead of phenylene-diamine, tolylene-diamine and other diamines may be made to react with diazobenzene nitrate; or again, instead of diazobenzene, diazotoluene, diazoxylene, &c., may be employed. The author has examined more particularly the product of the action of tolylene-diamine on diazotoluene. The base crystallises from alcohol in fine orange-yellow needles which melt at 183°. It forms easily crystallisable salts. The hydrochloride, $C_{14}H_{16}N_4.HCl$, resembles chrysoïdin. J. R.

Action of Benzotrichloride on Phenol. By O. DOEBNER and W. STACKMANN (*Deut. Chem. Ges. Ber.*, ix, 1918—1920).—Benzotrichloride is prepared by passing chlorine into toluene till the latter ceases to gain weight. The product is freed from hydrochloric acid by washing with water and an alkaline carbonate, and submitted to fractional distillation. Twenty grams of benzotrichloride are gradually added to a mixture of 30 grams of phenol with 20 grams of zinc oxide, the liquid being heated on the water-bath after each addition. The reddish-brown mass which is thus obtained, is extracted with ether, and the zinc chloride and oxide are removed by filtration. The residue left after distilling off the ether is treated with steam, and then crystallised from acetic acid. The crystals consist of colourless prisms, and agree in composition and properties with benzoylphenol $C_6H_5CO.C_6H_4OH$. This body melts at 134°, is slightly soluble in cold water, easily so in alcohol, ether, and acetic acid. When crystallised from a mixture of equal volumes of water and alcohol, the crystals consist of colourless, serrated, ramified plates; from acetic acid of large pointed prisms.

Merz and Grucarevic (*Berichte*, vi, 1245), by treating phenol with benzoyl chloride and zinc, obtained a body of the composition $C_{20}H_{14}O_3$, which they regard as the benzoate of a benzoylphenol, with a melting point of 112·5°. It remains to be seen whether the benzoylphenol of the authors forms a benzoic ether with similar properties. The action of benzotrichloride on phenol and zinc oxide is expressed by the equation:—

$$2C_7H_5Cl_3 + 2C_6H_6O + 3ZnO = 2C_{13}H_{10}O_2 + 3ZnCl_2 + H_2O.$$

The benzoyl group enters partly into the hydroxyl group of the phenol, with formation of the phenyl ether of benzoic acid, $C_6H_5.CO.OC_6H_5$, partly into the nucleus, with formation of the isomeric benzoylphenol, $C_6H_5.CO.C_6H_4OH$, but the conditions which favour the one or the other of these reactions are not determined. The perfect analogy between the synthesis of salicyl-aldehyde (formyl-phenol) $HCO.C_6H_4OH$, from chloroform, and that of benzoylphenol, $C_6H_5.CO.C_6H_4OH$, from benzotrichloride (phenylic chloroform) is very striking. On the other hand there is a clear relation between these bodies and the phthaleins. G. T. A.

Chlorinated Acetophenone. By R. DYCKERHOFF (*Deut. Chem. Ges. Ber.*, x, 119—121).—The author has obtained, by the action of potassium sulphocyanate on chlorinated acetophenone, an ether which crystallises from alcohol, ether, and chloroform in long needles having the composition expressed by the formula, $C_6H_5.CO.CH_2.S.CN$, and melting at 72—73°. This substance is apparently reduced by boiling its alcoholic solution with tin and hydrochloric acid, but the author has not succeeded in isolating any reduction-product.

In the process just mentioned there is formed a sparingly soluble body, which crystallises in delicate needles melting at 203—204°, and having the same composition as the ether melting at 72—73°, of which it is a polymeride. This body dissolves in soda-ley in the cold, and in ammonia on warming, and is precipitated from the solutions by hydrochloric acid.

The ether melting at 72—73° is decomposed by dilute nitric acid, yielding carbon dioxide, sulphuric acid, and benzoic acid.

J. R.

The Structural Formulæ of Hydroxylamine and its Amidated Derivatives. By W. LOSSEN (*Liebig's Annalen*, clxxxvi, 1—74).—The author has already demonstrated that two out of the three hydrogen atoms in hydroxylamine are unequal in function, inasmuch as anisbenzhydroxamic acid, $N\overset{1}{(C_8H_7O_2)}\overset{2}{(C_7H_5O)}HO$ is not identical with benzanishydroxamic acid and $N\overset{1}{(C_7H_5O)}\overset{2}{(C_8H_7O_2)}HO$: he now finds that the third hydrogen atom is dissimilar in function from either of the other two, since there can exist three different bodies in which two atoms of hydrogen are replaced by benzoyl and one by anisyl, and three in which two atoms are replaced by anisyl and one by benzoyl, *i.e.*, the three bodies—

Benzanisbenzhydroxylamine ..	$N\overset{1}{(C_7H_5O)}\overset{2}{(C_8H_7O_2)}\overset{3}{(C_7H_5O)}O$
Dibenzanishydroxylamine	$N\overset{1}{(C_7H_5O)}\overset{2}{(C_7H_5O)}\overset{3}{(C_8H_7O_2)}O$ and
Anisdibenzhydroxylamine	$N\overset{1}{(C_8H_7O_2)}\overset{2}{(C_7H_5O)}\overset{3}{(C_7H_5O)}O$

are all three different, as are also the three

Anisbenzanishydroxylamine ..	$N\overset{1}{(C_8H_7O_2)}\overset{2}{(C_7H_5O)}\overset{3}{(C_8H_7O_2)}O$
Dianisbenzhydroxylamine	$N\overset{1}{(C_8H_8O_2)}\overset{2}{(C_8H_7O_2)}\overset{3}{(C_7H_5O)}O$and
Benzdianishydroxylamine	$N\overset{1}{(C_7H_5O)}\overset{2}{(C_8H_7O_2)}\overset{3}{(C_8H_7O_2)}O$.

Not only do these different isomerides exist, but moreover each one of them is capable of crystallising in different forms differing in appearance and melting point (though not in chemical reactions), so that more than one modification of each isomeride exists; these modifications the author distinguishes as α, β, or γ *benzanisbenzhydroxylamine*, &c.

In order to prepare these bodies, benzoyl or anisyl chloride was made to react on the calculated quantity of the dry silver salt of the appropriate dihydroxamic acid, the materials being dissolved or suspended in benzene, and allowed to remain in contact at the ordinary temperatures until the decomposition of the silver salt was complete. The insoluble mass thus left consisted of the required tri-derivative (practically insoluble in benzene) mixed with silver chloride and more or less of the dihydroxamic acid, according to the greater or lesser purity of the organic chloride used. On boiling with alcohol and cooling the filtered solution, the tri-derivative separates as an oily or semi-solid mass, soon becoming crystalline, and only sparingly soluble in cold alcohol;

by redissolving in as little hot alcohol as possible, and pouring the solution into a soda solution, any adhering dihydroxamic acid is retained, and the tri-derivative obtained pure. By repeated crystallisation from ether, and separation by hand of the best shaped crystals thus obtained, the different kinds of crystals constituting the α, β, &c., modifications are separated and obtained pure: frequently crystals of measurable size and determinate characters are obtained only by spontaneous evaporation of the ethereal liquor.

In this way were obtained, from the silver salt of benzanishydroxamic acid and benzoyl chloride, three modifications of *benzanisbenzhydroxylamine*, all formed in virtue of the reaction—

$$N(C_7H_5O)(C_8H_7O_2)AgO + C_7H_5O.Cl = AgCl + N(C_7H_5O)(C_8H_7O_2)(C_7H_5O)O.$$

The *α-modification* crystallises in the triclinic system, and melts at 113—114°; this is the modification formed in largest quantity: the *β-variety* crystallises in rhombic form, melting at 124—125°, and is chiefly found in the alcoholic mother-liquors of the first crystallisation of the crude product of the reaction. The *γ-modification* crystallises in the monoclinic system together with the α-crystals, and is separable only by hand-picking: it appeared to melt at 110°; but after fusion and solidification (which required a week) it melted at 120°, indicating that by fusion it had become converted into the β-modification. In one preparation out of 46 grams of the three modifications jointly, 35 of the α, about 6 of the β, and about 5 of the γ variety were obtained.

When either of these modifications is heated with dilute hydrochloric acid, decomposition is brought about in accordance with the following reaction, benzanishydroxamic acid being formed—

$$(1.)\quad N(\overset{1}{C_7H_5O})(\overset{2}{C_8H_7O_2})(\overset{3}{C_7H_5O})O + H_2O = C_7H_6O_2 + N(\overset{1}{C_7H_5O})(\overset{2}{C_8H_7O_2})HO.$$

If, however, the acid be too strong or the action be too prolonged, more or less of the product becomes split up in accordance with the equation—

$$(2.)\quad N(C_7H_5O)(C_8H_7O_2)(C_7H_5O)O + 3H_2O = 2C_7H_6O_2 + C_8H_8O_3 + NH_3O.$$

The α-modification is partially split up, and chiefly in accordance with equation (1), by heating to 100° for half an hour with 8—10 parts of hydrochloric acid of sp. gr. 1·05; the β-modification suffers no change under these circumstances; nor is more than a small quantity decomposed if the acid have a sp. gr. of 1·14; by using fuming acid, however, it is decomposed, mostly in accordance with equation (2); benzhydroxamic acid formed in accordance with equation (1) was, however, separated from the products of the reaction. Modification-γ behaves as though it were a mixture of α and β, although its crystalline form negatives the supposition that such was its character; on heating with acid of sp. gr. 1·05 to 100°, it formed benzoic and benzhydroxamic acids like the α-modification, whilst a considerable residue remained unaltered, which on examination was found to be identical with the β-variety. Close upon 40 per cent. of the β body was thus obtained from the γ (selected well-defined crystals being used), far too large a quantity to be due to accidental admixture from imperfect separation of the two kinds of crystals.

Similarly, alcoholic potash decomposes each of the modifications α and β in accordance with the reaction—

$$N(\overset{1}{C_7H_5O})(\overset{2}{C_8H_7O_2})(\overset{3}{C_7H_5O})O + KO.C_2H_5 = C_7H_5O_2.C_2H_5 + N(\overset{1}{C_7H_5O})(\overset{2}{C_8H_7O_2})KO,$$

forming ethyl benzoate and potassium benzanishydroxamate. When aqueous caustic potash is used, the α-body is decomposed to a considerable extent in a similar way, forming potassium benzoate and benzanishydroxamate; but a different reaction also takes place to a small extent, forming potassium anisate and dibenzhydroxamate; whilst a little substance becomes yet further decomposed, forming a mono-hydroxamic acid.

On heating the α-modification it decomposes, with slight carbonization, in accordance with the reaction—

$$(1.)\quad N(\overset{1}{C_7H_5O})(\overset{2}{C_8H_7O_2})(\overset{3}{C_7H_5O})O = N.CO.C_6H_5 + C_7H_5O.O.C_8H_7O_2,$$

producing phenyl cyanate and benz-anisic anhydride, just as tribenzhydroxylamine forms phenyl cyanate and benzoic anhydride: a small portion also decomposes in accordance with the reaction—

$$(2.)\quad N(\overset{1}{C_7H_5O})(\overset{2}{C_8H_7O_2})(\overset{3}{C_7H_5O})O = N.CO.C_6H_4.O.CH_3 + C_7H_5O.O.C_7H_5O,$$

forming the cyanate of oxymethyl-phenyl, and benzoic anhydride. Quantitative estimations of the amount of benzoic acid finally produced by first heating a weighed quantity of α-benzanisbenzhydroxylamine in a sealed tube, and then again heating the products of the decomposition with strong hydrochloric acid, yielded 35·6 per cent., equation (1) requiring 32·5, and equation (2) twice as much: whence reaction (2) only occurs to a very small extent.

In precisely the same way as above described, *dibenzanishydroxylamine* was prepared and studied, the starting-point being the silver salt of dibenzhydroxamic acid and anisylchloride. *Modification* α: melts at 110—110·5°; crystals monoclinic; with hydrochloric acid of sp. gr. 1·05 easily splits up, forming anisic and dibenzhydroxamic acids. *Modification* β: melts at 109—110°; crystallises in rosettes, occurring with the last crops of crystals of α: crystalline system not determined: not attacked appreciably by hydrochloric acid of sp. gr. 1·05, but split up on long heating with acid of sp. gr. 1·14, dibenzhydroxamic acid being the only dihydroxamic acid produced: most of the substance, however, was wholly split up, forming benzoic and anisic acids and hydroxylamine.

The action of caustic potash on each of these modifications was different from what would naturally be expected: instead of the last introduced anisyl-group being eliminated, potassium benzoate and benzanishydroxamate were in each instance formed. The action of heat alone on α-dibenzanishydroxylamine is precisely the same as on the isomeric benzanisbenzhydroxylamine, *i.e.*, phenyl cyanate and benzanisic anhydride are the main products, whilst a little oxymethyl-phenyl cyanate and benzoic anhydride are also formed.

Similarly *anisdibenzhydroxylamine* was prepared from benzoyl chloride and silver anisbenzhydroxamate.

α-modification: melting-point 137—137·5°: monoclinic. Slowly decomposed by hydrochloric acid of sp. gr. 1·05, more readily by acid of sp. gr. 1·14, forming anisbenzhydroxamic acid: potash forms the same acid. On heating alone it forms oxymethyl-phenyl cyanate and benzoic anhydride in considerable quantity, and only small quantities of phenyl cyanate and benzanisic anhydride, behaving in this way just conversely with the two isomerides above described.

β-modification. Melts at 109·5—110·5°, crystallises in small rosettes of undetermined system. Not decomposed by hydrochloric acid of sp. gr. 1·05, and only partially attacked by acid of sp. gr. 1·14. With potash it forms anisbenzhydroxamic acid.

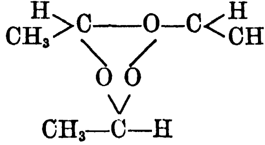
In precisely the same way three isomeric dianisated monobenzoylated hydroxylamines were prepared, two of which formed both α and β modifications.

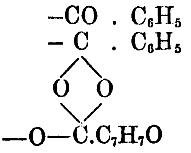
Anisbenzanishydroxylamine: from silver anisbenzhydroxamate and anisyl chloride.—*α-modification:* melts at 152—153°. Monoclinic. Hydrochloric acid of sp. gr. 1·05 readily splits it up forming anisic and anisbenzhydroxamic acids. Potash on the other hand forms benzoic and dianishydroxamic acids.—*β-modification:* melts at 148—149°. Monoclinic: formed only in very small quantity (0·5 gram as compared with 17 grams of α-modification).

Dianisbenzhydroxylamine, from silver dianishydroxamate and benzoyl chloride. Only one modification observed: melting at 147·5°. Monoclinic. Slowly attacked by hydrochloric acid of sp. gr. 1·05, more rapidly by stronger acid, forming benzoic acid and dianishydroxamic acid with no benzoylated hydroxamic acid of any kind. Caustic potash chiefly forms benzoic and dianishydroxamic acids, together with some anisic and anisbenzhydroxamic acids.

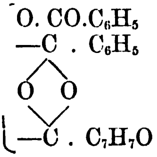
Benzdianishydroxylamine, from silver benzanishydroxamate and anisyl chloride.—*α-Modification:* melts at 137·5—138·5°. Triclinic. Hydrochloric acid of sp. gr. 1·05 forms anisic acid: potash gives anisic and benzanishydroxamic acids.—*β-modification:* melts at 137·5—138·5°. Triclinic. Hydrochloric acid of sp. gr. 1·05 forms anisic acid. Differs from the α-body only in the values of the angles of the crystals, the system being the same.

The author discusses at considerable length the foregoing observations and their bearings on the quantivalence of nitrogen and the functions of the different hydrogen-atoms in ammonia. Manifestly, so far as the action of hydrochloric acid is concerned, *the radicle last introduced so as to give rise to a tri-substituted hydroxylamine is the one first eliminated*, the other two remaining latest. The same rule often holds as regards the action of potash, but not at all invariably, benzanisbenzhydroxylamine and benzdianishydroxylamine being partial exceptions, and dibenzanishydroxylamine and anisbenzanishydroxylamine being entire exceptions to the rule: on the other hand, this rule is always observed, that *the radicle first introduced, forming a mono-substituted hydroxylamine, always remains last when the trisubstituted hydroxylamines derived from this mono-substituted hydroxylamine is decomposed by potash so as to eliminate two out of the three radicles.* In other words, a radicle is more energetically retained when in place 1 than in either place 2 or 3; but as regards these two places, the ease with which the radicle is eliminated depends on its nature: benzoyl seems to be more readily eliminated than anisyl when one of them is in one of the two places, 2 and 3, and the other in the other.

The occurrence of different modifications, α, β, γ, of a given tri-substituted hydroxylamine is explicable by supposing that these different bodies are simply polymeric; or that, just as aldehyde $CH_3.CHO$ forms a tripolymeride,  so bodies of the constitution:—



and



may exist different from the body $N\left\{\begin{array}{l}CO.C_6H_5\\ CO.C_6H_5.\\ O.CO.C_7H_7O\end{array}\right.$

Again, polymerism may be brought about by the nitrogen becoming pentadic, so as to give rise to a substitution-derivative of $\left.\begin{array}{l}HO\\ H_2\end{array}\right\}N{=}N\left\{\begin{array}{l}OH\\ H_2\end{array}\right..$

On the other hand, the author considers that the existence of the entirely different isomerides above described demonstrated *that the combining powers or valencies of a nitrogen atom are each one different from the other.*

C. R. A. W.

Phthalic Aldehyde. By A. BAEYER (*Deut. Chem. Ges. Ber.*, x, 123).—The author prepares this substance by dissolving 10 parts of phthalic chloride in dry carbon bisulphide, adding thereto 3 parts of phosphorus, also dissolved in carbon bisulphide, and passing over the liquid a slow current of hydrogen iodide, with frequent agitation. After 12 hours the carbon bisulphide is distilled off; the residual liquid is mixed with water to decompose the phosphorus iodide formed in the reaction, and the aqueous solution is shaken with ether, which takes up phthalic aldehyde, and leaves it in colourless tabular crystals on evaporation.

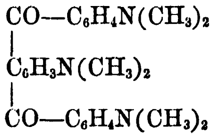
Phthalic aldehyde crystallises from water in colourless needles. In alkaline solution it is readily oxidised to phthalic acid by potassium permanganate. When boiled with potash, it is transformed into a new acid. Heated to 180—200° with hydriodic acid and red phosphorus, it is converted into a mixture of hydrocarbons, boiling between 112° and 120°, and intermediate in composition between toluene and xylene.

J. R.

Behaviour of Cuminol with Potash. By RICHARD MEYER (*Deut. Chem. Ges. Ber.*, x, 149—154).—The numerous investigations of cymene made of late years leave little doubt as to the identity of the various hydrocarbons of the formula $C_{10}H_{14}$, to which that name has been applied. Moreover, the formation of paratoluic acid and terephthalic acid by the oxidation of cymene, and the synthesis of cymene from propyl bromide and bromotoluene, show that the constitution of cymene is that of parapropylmethyl-benzene, (1 : 4) $C_6H_4{<}^{CH_3}_{C_3H_7}$. This view is, however, inconsistent with the statement of Kraut, that cymene is formed by the action of potash on cuminol.

The author has repeated Kraut's experiments, and finds that pure cuminol, when boiled with alcoholic potash, or when digested therewith in the cold, yields cuminic acid and cuminic alcohol, but no cymene. The cymene found by Kraut probably existed as such in the cuminol employed by him. Hence the author concludes that we know as yet only one cymene—paramethylpropylbenzene. J. R.

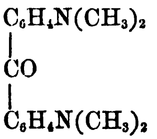
Synthesis of Ketones from Dimethylaniline. By W. MICHLER and C. DUPERTUIS (*Deut. Chem. Ges. Ber.*, ix, 1899—1901).—When dimethylaniline is heated almost to boiling, while chlorocarbonic acid is being passed into it, the latter is completely absorbed. As soon as the absorption ceases, the remaining dimethylaniline is removed by hydrochloric acid, and the product of the reaction is crystallised from hot alcohol. On evaporation of the solution, crystals of *hexamethyltriamidodibenzoylbenzene*,



$$\begin{array}{l}\mathrm{CO{-}C_6H_4N(CH_3)_2}\\ |\\ \mathrm{C_6H_3N(CH_3)_2}\\ |\\ \mathrm{CO{-}C_6H_4N(CH_3)_2}\end{array}$$

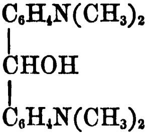
separate out. They melt at 122°.

For the preparation of *tetramethyldiamidobenzophenone*,



$$\begin{array}{l}\mathrm{C_6H_4N(CH_3)_2}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{C_6H_4N(CH_3)_2}\end{array}$$

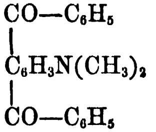
chlorocarbonic acid is passed at ordinary temperatures, and with frequent shaking, into a weighed quantity of dimethylaniline, till the increase of weight indicated by theory is reached. The product of the reaction (tinged with a blue colouring matter) is separated from the remaining dimethylaniline by boiling with water; by repeated solution in hydrochloric acid, and precipitation by caustic soda, the base is obtained in yellow flocks, which, when purified, melt at 179°. On heating this body in a stream of hydrochloric acid gas, a combustible gas is given off, which burns with a green flame. By the action of sodium amalgam on tetramethylamidobenzophenone, small crystals are obtained with a melting point of 96°. They probably consist of the corresponding benzhydrol,



$$\begin{array}{l} C_6H_4N(CH_3)_2 \\ | \\ CHOH \\ | \\ C_6H_4N(CH_3)_2 \end{array}$$

This body has basic properties, and dissolves in ether and alcohol, and also in acetic acid, with a deep blue colour, disappearing on addition of an alkali.

Action of Benzoyl Chloride on Dimethylaniline.—By heating 1 molecule of benzoyl chloride with 2 molecules of dimethylaniline either in a closed tube at 150—180°, or in a flask with an upright condenser, a body is obtained with the formula—



$$\begin{array}{l} CO—C_6H_5 \\ | \\ C_6H_3N(CH_3)_2 \\ | \\ CO—C_6H_5 \end{array}$$

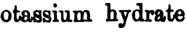
It is probably *dimethylamidodibenzoylbenzene.* It is soluble in alcohol and ether, and crystallises in beautiful crystals which melt at 55°. Its origin may be expressed by the following equation:—

$$C_6H_5N(CH_3)_2 + 2C_6H_5COCl =$$
$$2HCl + C_6H_5—CO—C_6H_3N(CH_3)_2—CO—C_6H_5.$$

G. T. A.

Synthesis of Organic Acids and Ketones by means of Chlorocarbonic Acid.

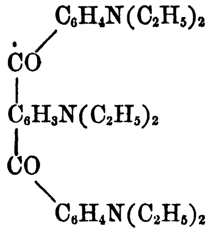
By W. MICHLER and A. GRADMAN (*Deut. Chem. Ges. Ber.*, ix, 1912—1915).—*Diethylamidobenzoic Acid.* Chlorocarbonic acid is passed at ordinary temperatures into diethylaniline till it ceases to be absorbed. The crystalline mass thus obtained is melted by a gentle heat, and again treated with chlorocarbonic acid. The product is mixed with water, and the excess of diethylaniline removed by acetic acid. After filtration, the colouring matter is separated by washing with alcohol, and the residue crystallised from alcohol. It consists of small yellow plates. The substance thus prepared is an amido-acid, which melts at 188°, and consists of



$$\begin{array}{l} C_6H_4N(C_2H_5)_2 \\ | \\ COOH. \end{array}$$

Paradiethylamidobenzoic Acid.—Potassium hydrate (3 molecules) is dissolved in alcohol and mixed with ethyl iodide (1 molecule) and paramidobenzoic acid (1 molecule). The mixture is heated for several hours, using an upright condenser, filtered off from the potassium iodide, and the filtrate evaporated. The residue is dissolved in acetic acid, when the diethylamidobenzoic acid separates mixed with traces of the mono-compound. To separate the two, they are converted into chlorides, and submitted to fractional crystallisation. The crystals which first appear consist of the hydrochloric acid salt of diethylamidobenzoic acid: the acid obtained from this melts at 188°, and resembles in all respects the acid prepared from diethylaniline.

Action of Diethylaniline on the Chloride of Diethylamidobenzoic Acid.—Diethylaniline is treated with chlorocarbonic acid as long as the gas is absorbed. Half the volume of diethylaniline is added, and the whole heated for some time to 120° in a sealed tube. A blue mass of crystals is thus obtained, which is freed from diethylaniline by boiling with water. The residue, when dissolved in hydrochloric acid, is deposited for the most part in crystals, but some of it passes into solution as a hydrochloric acid salt. The insoluble portion crystallises from alcohol in beautiful crystals which melt at 70°. The formula of this body is:—



It may be regarded as *hexethyltriamidodibenzoylbenzene.* The hydrochloric acid solution deposits the base on addition of caustic soda; it may be freed from adhering colouring matter by repeating the operation. When recrystallised from alcohol it is obtained in small plates which melt at 95—96°. The hydrochloric acid salt gives, with platinum chloride, a fine yellow double salt, of the composition:—

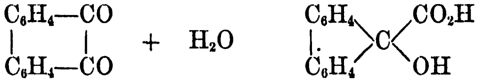
$$(C_6H_4N(C_2H_5)_2\text{—}CO\text{—}C_6H_4N(C_2H_5)_2) + 2HCl + PtCl_4.$$

The compound is, therefore, *tetrethyldiamidobenzophenone.* These two bodies may also be prepared separately. When diethylaniline is heated almost to boiling, while chlorocarbonic acid is being passed into it, hexethyltriamidodibenzoylbenzene is formed. If into a weighed quantity of diethylaniline chlorocarbonic acid is passed till the weight necessary for the formation of tetrethyldiamidobenzophenone is reached, this body is formed on boiling. The authors have also attempted to prepare benzoic acid from benzene and chlorocarbonic acid by heating them to 200° in presence of zinc-dust, but unsuccessfully: the ether of benzoic acid also gave no results.

When benzyl chloride and dimethylaniline are brought together at ordinary temperature, a hydrochloric acid salt of a new base separates out, which the authors are investigating. G. T. A.

Diphenyleneglycollic Acid. By P. FRIEDLANDER (*Deut. Chem. Ges. Ber.*, x, 125—127).—Phenanthrenequinone, when warmed with soda-ley, turns brown, and yields a brown solution, which becomes colourless after prolonged boiling. On addition of an acid, there is deposited a substance which crystallises from hot water in white laminæ melting at 161—162°. This product dissolves in warm strong sulphuric acid with fine indigo-blue colour, which disappears on addition of water. It dissolves easily in alkalis, and is precipitated unchanged by acids. The crystals dried over sulphuric acid have the composition expressed by the formula $C_{14}H_{10}O_3 + \frac{1}{2}H_2O$. The water is expelled at 80°. The calcium salt, $(C_{14}H_9O_3)_2Ca + 2H_2O$, forms colourless, sparingly soluble crystals.

The new acid is formed from phenanthrenequinone by assimilation of 1 mol. of water. Its constitution is not yet made out, but the author thinks it may probably be expressed as follows:—

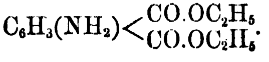


Phenanthrenequinone. Diphenyleneglycollic acid.

When heated with potassium chromate and sulphuric acid, the acid gives off carbon dioxide, and yields a substance which crystallises from alcohol, melts at 82°, and has the composition of diphenylene-ketone.

J. R.

Amidophthalic Acid. By W. KÖNIGS (*Deut. Chem. Ges. Ber.*, x, 124).—To prepare this substance the author proceeds as follows:—A solution of ethyl nitrophthalate (obtained by the action of hydrochloric acid on a hot solution of nitronaphthalic acid) in 2 vols. of alcohol, is mixed with 10 vols. of hydrochloric acid, of sp. gr. 1·09; the mixture is kept cool by means of ice, and zinc-dust is added gradually, till oily drops disappear and a distinct evolution of gas takes place. The liquid is then diluted with water and nearly neutralised with sodium carbonate, and sodium acetate is added, whereupon ethyl amidophthalate crystallises out. This product crystallises from ether in large, colourless, monoclinic prisms, agreeing in composition with the formula—



$$C_6H_3(NH_2)<\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix}.$$

Ethyl amidophthalate dissolves without change in hydrochloric acid, and is precipitated from the solution by alkalis or sodium acetate.

J. R.

Oxyterephthalic Acid. By G. A. BURKHARDT (*Deut. Chem. Ges. Ber.*, x, 144—149).—The author obtains oxyterephthalic acid by dissolving crystallised amidoterephthalic acid in soda-ley, acidifying the solution with sulphuric acid, adding the requisite quantity of potassium nitrite dissolved in water, and boiling.

The acid forms a white powder, easily soluble in alcohol and wood-spirit, but sparingly in water. At a high temperature it sublimes, with partial decomposition, without melting. Its aqueous solution gives with ferric chloride an intense, violet-red coloration, resembling that produced by salicylic acid.

The *silver salt*, $C_6H_3.OH.(COOAg)_2$, is white, and insoluble in water.

The *barium salt*, $C_6H_3.OH.(COO)_2Ba + Aq.$, crystallises from water in white laminæ.

Dimethyl oxyterephthalate, $C_6H_3\left\{\begin{matrix}COOCH_3\\COOCH_3\\OH\end{matrix}\right.$, is obtained by passing hydrogen chloride into a solution of the acid in methyl alcohol. It crystallises from methyl alcohol in beautiful silky needles, which melt at 94°. It dissolves in hot water, and easily in aqueous alkalis, alcohol, and ether. The solution in ammonia gives precipitates with salts of the heavy metals.

Dimethyl acetoxyterephthalate, $C_6H_3\left\{\begin{matrix}OC_2H_3O\\(CO_2CH_3)_2\end{matrix}\right.$, obtained by heating the dimethyl-ether to 100° with excess of acetyl chloride in sealed tubes, crystallises from alcohol in white, cauliflower-like masses, melting at 76°. It is insoluble in soda-ley.

Decompositions of Oxyterephthalic Acid.—1. When submitted to dry distillation, the acid is resolved into carbon dioxide and phenol.

2. When heated to 220° with hydrochloric acid in sealed tubes, it yields oxybenzoic acid. J. R.

Contributions to the Knowledge of the three Isomeric Oxybenzoic Acids.

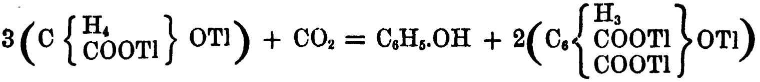
By A. von den Velden (*J. pr. Chem.* [2], xv, 151—172).—Ost having shown that normal potassium salicylate, when heated, yields carbonic anhydride, phenol, and basic potassium paraoxybenzoate, according to the equation—

$$2\left(C_6\left\{\begin{matrix}H_4\\COOK\end{matrix}\right\}OH\right) = C_6\left\{\begin{matrix}H_4\\COOK\end{matrix}\right\}OK + C_6H_5.OH + CO_2$$

Potassium salicylate. Basic potassium paraoxybenzoate.

and Kupferberg having shown that the sodium salt does not yield the paraoxybenzoate, but merely basic salicylate, the author undertook the examination of the action of heat on other salts of salicylic acid, at various temperatures, the heat being applied to the retort containing the salt by means of an oil or metal bath; in all cases he found that decomposition into phenol, carbonic anhydride, and a basic salt took place; in no case was an oxybenzoate obtained. The salicylic acid being recognised by its solubility in chloroform, by the violet reaction with ferric chloride, and by its melting point (156°), which is raised if paraoxybenzoic acid be present; paraoxybenzoic acid is insoluble in chloroform, and melts at 210°. If a mixture of oxy- with paraoxybenzoic acid occurs, it will be found that the oxy-acid crystallises anhydrous, the paraoxy-acid crystallising with one molecule of water. Lithium salicylate yielded only basic salicylate, and no trace of oxy- or paraoxybenzoate.

Rubidium is more closely allied to potassium than to sodium, and in combination with salicylic acid, yields when heated to 250°, the paraoxybenzoate, without a trace of salicylate. The decomposition of thallium salicylate is remarkable, for until the temperature reaches 220°, phenol passes over gradually, but directly that temperature is attained, violent reaction ensues, and the temperature rises suddenly 10—20°, and even up to 290° only basic salicylate is formed; but if the thallium salicylate be heated above 300°, a black mass, soluble in sulphuric acid is obtained, from which salicylic acid was extracted by chloroform, and on treatment of the residue with sodium carbonate, and an addition of acid to the solution thus obtained, phenol-dicarbonic acid was precipitated, paraoxybenzoic acid being obtained from the mother-liquor. The formation of the dicarbonic acid is evidently due to the reaction of the liberated carbonic anhydride reacting on the basic salt thus:—



$$3\left(C\left\{\begin{matrix}H_4\\COOTl\end{matrix}\right\}OTl\right) + CO_2 = C_6H_5.OH + 2\left(C_6\left\{\begin{matrix}H_3\\COOTl\\COOTl\end{matrix}\right\}OTl\right)$$

and that such is probably the case is supported by the fact that if the neutral salt be heated in an atmosphere of hydrogen, the formation of phenol-dicarbonic acid still takes place. For want of a supply of cæsium, no experiments with its salts could be made. Salts of several other metals were experimented on, but the salicylic acid was not transformed. In the case of the ferric salt, it was changed at 260° into a black, resinous mass; the copper and silver salts at a lower temperature were reduced to the cuprous salt and metallic silver respectively.

Action of Sodium-amalgam on the three Isomeric Oxybenzoic Acids.—Salicylic acid is not reduced by nascent hydrogen in an alkaline solution, but in an acid solution it yields saliretin, and not saligenin; with a neutral solution no result was obtained. Paraoxybenzoic acid behaves in like manner to salicylic acid, when heated with nascent hydrogen. Oxybenzoic acid in an alkaline solution is unaffected, but if the solution be acid, oxybenzyl alcohol [benzyl glycol], an uninvestigated acid, and unaltered oxybenzoic acid may be dissolved out by ether from the resulting solution. The oxybenzyl alcohol thus obtained is a thick, slightly yellow oil, which solidifies over sulphuric acid in a vacuum to a white crystalline mass.

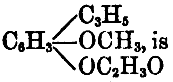
Oxybenzyl alcohol, $C_6\left\{\begin{matrix}H_4\\OH\end{matrix}\right\}$—$CH_2OH$, is a colourless, odourless solid, resembling phenol in appearance, melting at 67°, and boiling at 300°, with partial decomposition; it is slightly soluble in cold, but easily in hot water; soluble also in alcohol and ether; sparingly soluble in chloroform. With ferric chloride it gives a violet coloration, which on further addition of ferric chloride changes to greyish-brown. Oxybenzyl alcohol is not oxidised by potassium bichromate and sulphuric acid, nor by potassium permanganate, but yields potassium oxybenzoate (m. p. 200°) on fusion with potash. As benzyl alcohol when boiled with alcoholic potash yields benzoic acid and toluene, it seemed probable that oxybenzyl alcohol would in like manner yield oxybenzoic acid and cresol; but experiment shows that this is not the case, the oxybenzyl alcohol remaining unattacked.

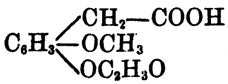
Treated with glacial acetic acid and sulphuric acid, oxybenzyl alcohol is converted into *normal, oxybenzylic acetate,* $C_6\left\{\begin{matrix}H_4\\OH\end{matrix}\right\}CH_2O.C_2H_3O$, which appears as an oil, insoluble in water, solidifying on drying to a solid yellow mass, which melts at 55°, and boils with partial decomposition, at 295—302°. This ether is but slightly soluble in water, but dissolves readily in alcohol and ether, and yields a violet coloration with ferric chloride.

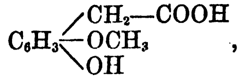
Acid oxybenzylic acetate, $C_6\left\{\begin{matrix}H_4\\O.C_2H_3O\end{matrix}\right\}CH_2C_2H_3O$, is obtained when an excess of acetic anhydride is heated in sealed tubes with oxybenzylic alcohol: it is a liquid solidifying at − 18°, insoluble in water, but soluble in alcohol and ether, possessing a pungent odour, and boiling at 290°. An attempt to produce the third ether, $C_6\left\{\begin{matrix}H_4\\O.C_2H_3O\end{matrix}\right\}CH_2OH$, by careful saponification was fruitless, oxybenzylic alcohol being always obtained. Metallic potassium and sodium acting on oxybenzylic alcohol dissolved in dry ether, produce white hygroscopic solids, which have no constant composition. Hydrochloric acid transforms the alcohol into a resinous body, from which a chlorinated compound has been obtained, but not pure enough for analysis.

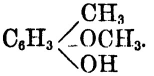
E. W. P.

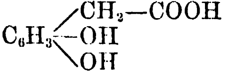
Alphahomovanillic Acid and Derivatives. By FERD. TIEMANN and NAGAJOSI NAGAI (*Deut. Chem. Ges. Ber.*, x, 201—213).—The authors have previously shown that when aceteugenol suspended in dilute acetic acid, is oxidised with potassium permanganate, acetovanillic acetate and acetovanillin are formed. Besides these substances however, there is produced, under some circumstances, a third body, acet-alphahomovanillic acid, which is described below.

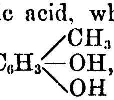
Aceteugenol,  $C_6H_3\begin{cases}C_3H_5\\OCH_3\\OC_2H_3O\end{cases}$, is formed by boiling together equal weights of eugenol and acetic anhydride. It is a crystalline, transparent substance, melting at 30—31°, and dissolving easily in alcohol and ether, but not in water or dilute alkalis. It is resolved by boiling potash into eugenol and acetic acid.

Acet-alphahomovanillic acid,  $C_6H_3\begin{cases}CH_2—COOH\\OCH_3\\OC_2H_3O\end{cases}$. This substance is formed, together with acetovanillic acid, on adding gradually a warm solution of 50 grams of potassium permanganate in 2000 c.c. of water, to a solution of 15 grams of aceteugenol in 20 c.c. of glacial acetic acid. It crystallises in transparent prisms, which dissolve easily in boiling water, alcohol, and ether, and melt at 140°. When heated above its melting point for some time, it gives off acetic acid, and yields alphahomovanillic acid. By prolonged fusion with potassium hydrate, it is converted into protocatechuic acid. Its solution in acetic acid is converted by oxidation with potassium permanganate into acetovanillic acid.

Alphahomovanillic acid,  $C_6H_3\langle\begin{matrix}CH_2—COOH\\ OCH_3\\ OH\end{matrix}$, is formed, as stated above, when a solution of acet-alphahomovanillic acid in soda-ley is heated for some time. It crystallises from boiling water or benzene in distinct hexagonal prisms, which melt at 142—143°, and dissolve easily in alcohol and ether. Its aqueous solution is coloured green by ferric chloride. The acid forms crystallisable and easily soluble ammonium, sodium, calcium, and barium salts, and sparingly soluble lead, silver, and zinc salts, in which the hydrogen of the carboxyl-group of the acid is replaced by the respective metallic radicles. It appears also to form another class of salts, in which the hydrogen of the hydroxyl of the benzene-residue is likewise replaced, but these are obtained with difficulty. Solutions of the alkali-salts do not reduce Fehling's solution.

Kreosol (*homoguaiacol*),  $C_6H_3\langle\begin{matrix}CH_3\\ OCH_3\\ OH\end{matrix}$. This substance, one of the constituents of beechwood tar, is formed by elimination of carbon dioxide, when the calcium salt of alphahomovanillic acid is mixed with calcium hydrate and sand, and submitted to dry distillation. It is more easily obtained in the pure state by this process than by treatment of the tar, which yields it only with extreme difficulty.

Alphahomoprotocatechuic acid,  $C_6H_3\langle\begin{matrix}CH_2—COOH\\ OH\\ OH\end{matrix}$, is formed when alphahomovanillic acid is heated to 170—180°, with dilute hydrochloric acid in sealed tubes. It crystallises in brilliant transparent needles, which melt at 127°, and dissolve easily in water, alcohol, and ether. It yields well-characterised crystallisable salts by substitution of metallic radicles for the hydrogen of the carboxyl-group. Basic salts also are formed by the further replacement of hydrogen in the hydroxyl-group, but they appear to be unstable.

The calcium salt of alphahomoprotocatechuic acid, when distilled with calcium hydrate, yields *homopyrocatechin*,  $C_6H_3\langle\begin{matrix}CH_3\\ OH\\ OH\end{matrix}$, a colourless, uncrystallisable, thick liquid, which dissolves easily in water, alcohol, ether, and benzene, and closely resembles pyrocatechin in chemical properties.

J. R.

Resorcintrisulphonic Acid. By J. PICCARD and A. HUMBERT (*Deut. Chem. Ges. Ber.*, x, 182).—Resorcindisulphonic acid, when heated to 200° for some hours with fuming sulphuric acid in a sealed tube, is converted into trisulphonic acid.

The free acid has not been obtained in crystals, owing to its easy solubility.

The *barium salt* forms snow-white microscopic crystals, agreeing in composition with the formula,—

$$H(OH)_2C_6 : (SO_2.O.Ba.O.SO_2)_3 : C_6(OH)_2H.$$

The *ammonium salt*, formed by digesting the barium salt with ammonium carbonate, produces crystalline precipitates in solutions of barium, lead, and calcium salts. J. R.

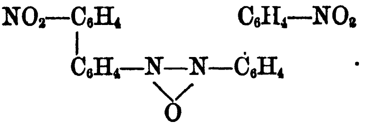
Decomposition of Oil of Turpentine at a high Temperature. By G. SCHULTZ (*Deut. Chem. Ges. Ber.*, x, 113—118).—The author obtained, by passing the vapour of oil of turpentine through an iron tube heated to dull redness, a tarry distillate, in which he found the following substances: benzene, toluene, xylene (chiefly 1 : 3), unaltered oil of turpentine, naphthalene, phenanthrene, anthracene, and methylanthracene. Carbon was deposited in the tube, and a large quantity of combustible gases (which were not examined) was produced.

J. R.

Pimaric Acid. By BRUYLANTS (*Chem. Centralb.*, 1876, 630).—The author confirms Laurent's formula for pimaric acid. The calcium salt, when distilled, yields gaseous hydrocarbons, among which are propene and amylene, and a liquid consisting of a hydrocarbon, C_5H_{10}, propione, $C_5H_{10}O$, and terebene. The hydrocarbon, C_5H_{10}, combines directly with bromine to form a dibromide, $C_5H_{10}Br_2$. The propione on oxidation with chromic acid gave propionic acid. Sodium pimarate, on dry distillation, also gave propionic acid. These decompositions show that pimaric acid is related to turpentine, which may be viewed as a hydride of cymene, which, in its turn, is related to propyl.

W. R.

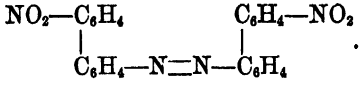
Azo-compounds of Diphenyl. By HEINRICH WALD (*Deut. Chem. Ges. Ber.*, x, 137—140).—Paradinitrophenyl, when suspended in alcohol and treated with sodium amalgam, is converted into a red powder, which, after purification, agrees in composition with the formula $C_{24}H_{16}N_4O_5$. This substance is regarded by the author as *paradinitro-azodiphenyl*,—



$$\begin{array}{lcl} NO_2\!-\!C_6H_4 & & C_6H_4\!-\!NO_2 \\ \quad | & & \quad\;\; | \\ C_6H_4\!-\!N & - & N\!-\!C_6H_4 \\ & \diagdown\!\diagup & \\ & O & \end{array}$$

It forms a brick-red crystalline powder, insoluble in most liquids, but readily soluble in boiling aniline. It melts at 225°, dissolves with fine deep red colour in strong sulphuric acid, and forms with strong nitric acid a yellow compound, insoluble in alcohol and ether, but soluble in benzene. By reduction with tin and hydrochloric acid, or with alcoholic ammonium sulphide at 115°, it yields benzidine melting at 122°.

Isodinitrophenyl reacts with alcohol and sodium amalgam to form a substance which dissolves sparingly in alcohol, easily in chloroform and benzene. This product melts at 187°, and agrees in composition with the formula $C_{24}H_{16}N_4O_4$, whence it may be regarded as *isodinitroazodiphenyl*,—



$$\begin{array}{lll} NO_2—C_6H_4 & & C_6H_4—NO_2 \\ \quad\;\; | & & \;| \\ \quad\;\; C_6H_4—N{=}N—C_6H_4 & & \end{array}$$

J. R.

Chrysin, Tectochrysin, and higher Homologues. By J. PICCARD (*Deut. Chem. Ges. Ber.*, x, 176—180).—The author has previously shown that there exists in the buds of the poplar, together with chrysin, another body to which he gave the provisional name tectochrysin. The latter body he found to be the next higher homologue of chrysin.

He has now succeeded in forming tectochrysin artificially by the introduction of the methyl-radicle into chrysin. This is effected by treating chrysin dissolved in methyl alcohol with ethyl iodide, and boiling the resulting product with potash. The tectochrysin (methylchrysin) thus formed is readily separated from unaltered chrysin by means of chloroform, in which the latter is not soluble.

Ethyl- and amyl-chrysin are obtained in a similar manner.

Methylchrysin crystallises from alcohol in transparent, sulphur-yellow, thick clinorhombic prisms melting at 164°.

Ethylchrysin forms long, silky, thin needles melting at 146°.

Amylchrysin from amylic alcohol of fermentation, likewise forms thin needles which melt at 125°.

Dibromamylchrysin, $C_{15}H_7Br_2(C_5H_{11})O_4$, formed by evaporating a solution of bromine and amylchrysin in chloroform, crystallises in fine needles.

Methyl-, ethyl-, and amyl-chrysin all dissolve sparingly in alcohol, easily in benzene and carbon bisulphide, and with great facility in chloroform, and are thereby perfectly distinguished from chrysin.

Chrysin dissolves in alkalis with deep yellow colour, and is resolved by prolonged boiling therewith into phloroglucin, acetic and benzoic acids, and methylphenyl ketone; whereas the above-named derivatives are not soluble in, and are very slowly attacked by alkalis. It follows, therefore, that chrysin is a phenol, of which the methyl and other derivatives are ethers, and that chrysin contains only one hydroxyl-group.

J. R.

Action of Ammonia on Alizarin. By HUGO R. v. PERGER (*J. prakt. Chem.* [2], xv, 224—228).—If alizarin be heated to 180—200° with a large excess of ammonia, the amount of alizaramide obtained decreases, more of a black insoluble compound being formed, which appears to be identical with the alizarimide described by Liebermann and Troschke. The contents of the tube were diluted, filtered, dried, and treated with alcohol. The alcoholic solution was evaporated and weighed. The aqueous filtrate was treated with pure hydrochloric acid, and the precipitated brown mass washed and digested with baryta-water; on addition of an acid, a beautiful red precipitate of alizaramide came down. This substance, on treatment with nitrous acid, gave pure monoxyanthraquinone. The black amorphous substance, insoluble in ammonia, was insoluble in water and in cold soda, but dissolved in alcohol with a blue colour; addition of water precipitated it in blackish-blue flocks, which, when dry, had a metallic lustre. On addition of caustic soda to the alcoholic solution, it turned violet-red: this colour was produced also by hydrochloric acid. When it was heated with caustic soda, ammonia was evolved, and on addition of hydrochloric acid, a body was precipitated in brown flocks, which evolved ammonia only when heated with soda-lime. These reactions were also given by the substance insoluble in baryta-water. Nitrous acid was then passed through the alcoholic solution of the blue substance; it turned first red, then brownish-yellow. The liquid was then diluted with water, when fine yellow flocks separated, which dissolved with difficulty in soda, forming a reddish-yellow solution. With baryta it gave a violet-red lake, totally insoluble in cold water; in ammonia it was quite insoluble. It was easily soluble in alcohol, ether, and glacial acetic acid, and melted at 180°. It could be sublimed and distilled. When fused with caustic potash it gives alizarin. These properties leave no room for doubt that this body is identical with the erythroxyanthraquinone obtained by Bayer and Caro from phthalic anhydride and the hydroxyl derivatives of benzene. The black substance insoluble in alcohol gave similar reactions when treated with caustic potash. The body which is difficultly soluble in baryta-water is the amide of erythroxyanthraquinone, which the author calls for shortness' sake β-alizaramide. As the insoluble black substance, when heated with caustic soda, evolves ammonia, the β-amide being formed, and as the β-amide is much more soluble in ammonia than the black substance, the latter is probably alizarindiamide. The author is pursuing this investigation. W. R.

Morphine Hydriodide and Hydromide. By ERNST SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 194).—The somewhat discordant statements in books as to the solubility and composition of morphine hydriodide prepared by different methods have induced the author to examine this substance afresh. He has prepared it by dissolving morphine in hydriodic acid, and by decomposing morphine acetate with potassium iodide, and finds that the products of these two processes are identical. The hydriodide crystallises in stellate groups of long silky needles, having the composition $C_{17}H_{19}NO_3HI + 2H_2O$. The water is given off at 100°, but is re-absorbed on exposure to air. The crystals are sparingly soluble in cold, and more freely in hot water.

Morphine hydrobromide, $C_{17}H_{19}NO_3HBr + 2H_2O$, prepared by neutralising hydrobromic acid with morphine, crystallises in tufts of long needles, which lose their water at 100°. J. R.

Cinchonine. By H. WEIDEL (*Chem. Centr.*, 1876, 597—599).—Four acids formed by the oxidation of cinchonine with nitric acid have already been described. Another product of basic character has since been obtained, which gives the following crystalline salts:—

Hydrochloride ...... $C_{16}H_{18}N_2O_5 . HCl$.
Platino-chloride...... $C_{16}H_{18}N_2O_5 . 2HCl . PtCl_4$.
Nitrate .... $C_{16}H_{18}N_2O_5 . HNO_3$.
Sulphate ....$2(C_{16}H_{18}N_2O_5) . H_2SO_4$.

The most remarkable reaction of the free base, as well as of its salts, is its power of reducing Fehling's solution, even if concentrated, in the cold. This reaction would make it appear to be the same substance that Caventou and Wilm obtained by acting on cinchonine with potassic permanganate. F. J. L.

Note on Weddell's Paper concerning the Substitution of Cinchonidine for Quinine. By L. PASTEUR (*Compt. rend.*, lxxxiv, 577—578).—Weddell erroneously attributes the discovery of cinchonidine to Pasteur. The facts are as follows:—In 1833 Messrs. Henry and Delondre discovered an alkaloïd which they termed *quinidine*, and described as isomeric with quinine. In 1848 Winckler discovered an alkaloïd which he likewise termed *quinidine*. In 1853 Pasteur demonstrated that this latter substance was isomeric with cinchonine, and therefore gave it the name *cinchonidine*. F. J. L.

Rapid Extraction of Caffeine. By PAUL CAZENEUVE and O. CAILLOL (*Bull. Soc. Chim.* [2], xxvii, 199—200).—Black tea is treated with four times its weight of boiling water, and when the leaves are softened, an amount of freshly slaked lime (equal to the weight of tea originally taken) is added, and the whole well mixed and evaporated to dryness on a water-bath. The residue is then placed in the exhausting apparatus recommended by one of the authors (Paul Cazeneuve. *Extraction des Alcaloïdes.* Delahaye, 1875), and exhausted by means of chloroform; the extract thus obtained is evaporated to dryness; and the resinous matter precipitated by treating the residue with boiling water. On carefully evaporating the filtered aqueous solution, beautiful silky white crystals of caffeine are obtained. C. A. B.

Gelsemium Sempervirens. By C. A. ROBINS (*Chem. Centr.*, 1876, 444).—The important constituents of the roots of this plant were stated by Wormsley to be about 0·1 per cent. of a highly poisonous alkaloïd, *gelsemine*, and about 0·04 per cent. of a peculiar acid, *gelsemic acid.*

The author disputes the existence of this acid, his experiments leading him to believe that the reactions attributed to it are really due to the presence of aesculin.

The alkaloïd gelsemine has the composition $C_{11}H_{19}NO_2$. A solution in concentrated sulphuric acid gives with potassic bichromate a cherry-red colour changing to violet. F. J. L.

Constituents of Cubebs. By ERNST SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 188—191).—Fresh analyses of the stearoptene of cubebs confirm the results arrived at by the author some ten years ago, when he found the stearoptene to have the formula, $C_{15}H_{26}O = C_{15}H_{24} + H_2O$, which is that of a hydrate of the oil of cubebs.

This conclusion as to the nature of the stearoptene is borne out by the fact that perfectly dehydrated oil of cubebs, when distilled, always yields water, which is probably derived from stearoptene dissolved in it. The stearoptene also yields water when heated to 250° in sealed tubes, or even when simply distilled. When kept over sulphuric acid, it slowly melts and becomes transformed into a perfectly transparent oily liquid, which boils at 250—260°, the boiling-point of oil of cubebs. J. R.

Properties of Albumin containing very small Quantities of Salts. By H. HAAS (*Chem. Centr.*, 1876, 795—800, 811—816, and 824—832).—Solutions of albumin freed as far as possible from salts, become strongly opalescent on addition of alcohol, or on boiling: in many cases, the solutions become turbid, and even throw down precipitates.

In this observation the author agrees with Heynsius, as opposed to Schmidt and Aronstein.

In its chemical behaviour pure albumin differs in no respect from that form of albumin which occurs in white of egg: it undergoes coagulation under the same conditions as are noticed when experimenting with egg-white.

The precipitation of albumin in flocks by means of hydrochloric acid or acid phosphates, is closely related to the proportion existing between the amounts of albumin and precipitant, and is entirely independent of the degree of concentration. The author regards the precipitation of albumin by acids in the form of flocks as a chemical process. The precipitation by salts is dependent upon the amount of water in the solution, and is probably only a physical action.

The author cannot offer a decided opinion as to the normal reaction of albumin at the close of a long process of dialysis. He has often obtained albumin showing an acid reaction, when the same albumin originally contained alkalis or alkaline carbonates; but such solutions he has shown to contain globulin, and he imagines that the acid reaction may be due to those substances, which act as solvents of the globulin. That pure albumin has a neutral reaction appears most probable.

The author regards the hypothesis of Heynsius, that albumin is a soluble compound of globulin with earthy phosphates, as unfounded. He is more inclined to favour Schmidt's view that albumin is maintained in solution by earthy phosphates, and that albumin perfectly free from salts has not as yet been obtained. M. M. P. M.

On Certain Phosphorescent Bodies. By BR. RADZISZEWSKI (*Deut. Chem. Ges. Ber.*, ix, 321).—The author has already shown that, on treating certain bodies with caustic potash and oxygen, light is evolved as a phosphorescence. These bodies all belong to the class of aldehydes or aldehyde derivatives; thus paraldehyde, metaldehyde, aldehyde-ammonia, furfurine, hydranisamide, anisidine, hydrocinnamide and hydrocuminamide, all show the reaction. In order to see if formic aldehyde and glucose would behave similarly, these bodies were examined; the latter gave a feeble but distinguishable phosphorescence when oxygen was passed through its alcoholic solution containing caustic potash; the former, prepared by the dry distillation of calcium formate and reception of the evolved vapours in a Liebig's bulb filled with alcohol, showed a stronger phosphorescence on treatment with oxygen in the same way. Still better results were obtained with the so-called dioxymethylene (polymeride of formic aldehyde) prepared by Heintz's process from calcium diglycollate and concentrated sulphuric acid. Duchemin has shown that the *Noctiluca milicris* produces on a tender hand the same effect as a stinging-nettle; possibly the phosphorescence is due to the excretion of formic aldehyde, and its atmospheric oxidation to formic acid which produces the smarting. Neurine does not give any phosphorescence. C. R. A. W.

Physiological Chemistry.

Action of Sodic Hyposulphite on the Hæmatin of Blood. By P. Cazeneuve (*Bull. Soc. Chim.* [2], xxvii, 258—260).—By the action of zinc upon sodic bisulphite out of contact of air, sodic hyposulphite is produced. Sodic hyposulphite decolorises indigo, reduces the salts of copper, and converts oxy-hæmoglobin into reduced hæmoglobin. If a few drops be added to an alkaline solution of hæmatin, the characteristic dichroic tint becomes replaced by a vermilion-red colour, and the spectroscopic band peculiar to the same solution disappears and is succeeded by a characteristic spectrum. H. H. B. S.

Conversion of Carbonyl-hæmoglobin into Oxyhæmoglobin. By C. Liman (*Chem. Centr.*, 1876, 388).—Eulenberg and Donders, by passing air through blood containing carbonyl hæmoglobin, succeeded in converting it into oxyhæmoglobin, but failed to do so by shaking the blood in a closed vessel.

This failure was due to the limited quantity of air thus brought in contact with the blood; for if the blood be poured from glass to glass for some time, complete conversion takes place. The fact that the blood from the body of men killed by carbonic oxide exhibits the characteristic spectra of carbonyl-hæmoglobin, whilst that from the body of one who has recovered from the effects of the gas does not, shows that the carbonic oxide is removed simultaneously with the process of resuscitation. F. J. L.

On the Normal Presence of Copper in the Blood of Wild Graminiverous Animals. By M. S. Cloez (*Bull. Soc. Chim.* [2], xxvii, 196—198).—The author obtained 530 grams of blood from the heart of a roebuck a few moments after death, collecting it in a porcelain basin, and transferring it to a flask for further examination. The plasma was then separated from the globules, and the latter evaporated down to dryness in a platinum crucible and carefully incinerated; the temperature not being allowed to rise high enough to volatilise the alkaline chlorides. The soluble portion was then separated by treatment with water, the insoluble residue dissolved in hydrochloric acid, and the excess of acid evaporated off. An excess of ammonium sulphide was then added to the solution, causing a copious black precipitate containing the copper sulphide and iron sulphide, the latter being subsequently removed and the copper sulphide estimated as cupric oxide. Only 3 mm. of cupric oxide were obtained from 530 grams of blood. The author cannot assign any reason for the occurrence of copper in the blood, but considers it important that medical men, when pursuing chemico-legal investigations, should not neglect to take into account the small quantities of copper sometimes occurring in normal blood. C. A. B.

Action of Bile on Peptones. By J. MOLESCHOTT (*Chem. Centr.*, 1876, 358).—When bile is added to a peptone, a precipitate ensues. This precipitate is soluble in an excess of about 4 or 5 times the volume of bile. The mucin of the bile does not participate in the action, for if it be first precipitated by addition of hydrochloric acid, and the liquid subsequently made alkaline, about 3—5 vols. of the bile so treated are sufficient to re-dissolve the precipitate from 1 vol. of peptone. F. J. L.

Fat-forming Equivalent of Albuminoïds. By HENNEBERG (*Chem. Centr.*, 1876, 821).—The author estimates, from experimental data, the fat-forming power of albuminoïds as 51·4 parts of fat per 100 of albuminoïd. M. M. P. M.

Nutritive Value of the Cellular Tissue of Plants. By E. REICHARDT (*Chem. Centr.*, 1876, 631).—The encrusting matter of cellular tissue is soluble partly in acids and partly in alkalis. In dilute hydrochloric acid (1 p.c.), 58·7 p.c. dissolves, and the residue, when treated with caustic soda of 1 p.c., yields 34·5 p.c. in solution, together, 93·2 p.c. This soluble matter is digestible, and the experiments show that such residues, after extraction of sugar, &c., are still useful as food. W. R.

Thiocyanates in Urine. By J. MUNK (*Chem Centr.*, 1876, 822). —Reactions of urine pointing to thiocyanic acid are detailed. The quantity of this acid in 100 c.c. of urine was determined, and found to be 0·008 gram = 0·011 gram sodium thiocyanate.
M. M. P. M.

A Peptone-forming Ferment in Saliva. By J. MUNK (*Chem. Centr.*, 1876, 822).—Reactions are enumerated, showing the presence in small quantity of a ferment in saliva which transforms fibrin into a peptone. M. M. P. M.

Chemistry of Vegetable Physiology and Agriculture.

Contributions to our Knowledge of Vegeto-chemical Phenomena. By A. EMMERLING (*Deut. Chem. Ges. Ber.*, x, 650—654).—Oxalic acid acts in dilute solution on calc-spar, but if a trace of nitric acid be added, the reaction proceeds much more quickly, the reason being that the calcium nitrate formed is at once decomposed by the oxalic acid, and thus the nitric acid acts like a ferment. In one series of experiments, equal quantities (*i.e.*, equal surfaces, were treated for 165 hours with 750 c.c. of solutions containing per litre:

	1	2	3
	$\frac{1}{100}$ mol. $C_2H_2O_4$.	$\frac{1}{1000}$ HNO_3.	$\frac{1}{100}$ $C_2H_2O_4$ and $\frac{1}{1000}$ HNO_3.
Loss of calc-spar..	trace	0·0330	0·1300

A second series gave, after 70 hours—

	1	2	3
	$\frac{1}{100}$ mol. $C_2H_2O_4$.	$\frac{1}{5000}$ HNO_3.	$\frac{1}{100}$ $C_2H_2O_4$ + $\frac{1}{5000}$ HNO_3.
Loss............	0·0040	0·0060	0·0240

In a former communication, the author stated that the nitrates of the alkalis are decomposed by oxalic acid in dilute solutions. This is proved by the following experiments:—

(1.) While a dilute solution of oxalic acid, or one of nitre, hardly acts on calc-spar, 750 c.c. of a solution containing per litre, $\frac{1}{100}$ mol. oxalic acid and $\frac{1}{1000}$ mol. nitre, decomposed in 72 hours 0·0690, in 120 hours, 0·0820, and in 214 hours, 0·1285 calc-spar.

(2.) By using, under the same conditions, a solution of $\frac{1}{20}$ mol. of oxalic acid and $\frac{1}{100}$ mol. of nitre, 0·3055 calc-spar was decomposed in 72 hours.

These experiments show that certain salts impart to oxalic acid the power of decomposing insoluble compounds which are hardly attacked by the pure acid. It appears highly probable that such reactions play a part in the functions of the roots which contain free acids, and come into contact with the soluble salts in the soil, and are thus enabled to decompose its insoluble constituents. C. S.

Absorption of Carbonic Acid by Vegetable Cell-walls. By J. BÖHM (*Chem. Centr.*, 1876, 808).—This absorption takes place out of direct sunlight. Branches dried at 100° absorb more carbonic acid than fresh branches. The carbonic acid can be slowly replaced in the dry branches, but quickly in the fresh, by oxygen, hydrogen, or nitrogen. M. M. P. M.

Rise of Sap in Plants, &c. By J. BÖHM (*Chem. Centr.*, 1876, 808).—The author reiterates his belief that rise of sap is a function of transpiration, of the elasticity of the cell-walls, and of the pressure of the air. M. M. P. M.

Influence of Light and of Radiant Heat on the Transpiration of Plants. By WIESNER (*Chem. Centr.*, 1876, 679).—Both luminous and non-luminous rays intensify the transpiration of plants. The influence of the ultra-violet rays was not perceptible. A gas-flame, burning under a pressure of 13 mm. of water, the illuminating power of which was equal to 6·5 spermaceti candles, was compared with sunlight. The influence of the dark heat-rays in the case of the flame bore to the action of the same rays of the sun the proportion of 57 to 21. The action of light results from its conversion into heat by being absorbed by the chlorophyll. This was proved in three different ways; by comparing the transpiration of green and yellow leaves in light; by transpiration in the spectrum; and by transpiration behind a solution of chlorophyll. Chlorophyll accelerates the rate of transpiration enormously; the parts of the spectrum which contain the black chlorophyll bands are most active in promoting transpiration; light rays which have passed through a solution of chlorophyll, have a very slight action, for the active parts of the light are absorbed. Chlorophyll has the greatest action of all colouring matters, but some others, *e.g.*, etiolin, are not without action. W. R.

On the Digestion of the Perisperm (Albumen). By PH. VAN TIEGHEM (*Compt. rend.*, lxxxiv, 578—584).—To investigate the method by which the perisperm is dissolved and absorbed by the embryo, two methods were employed. First, the perisperm separated from the integuments and embryo, was subjected to the ordinary conditions of germination to see if it would dissolve of itself. Secondly, the germination of the whole seed and the progress of the solution of its perisperm was watched to see whether this solution would be greater near the embryo, and so indicate an influence exerted by it. The effects produced in either case were found out by examining sections of the perisperm with the microscope.

The results obtained differ according to the composition of the perisperm, so that it is necessary to distinguish between oleaginous, farinaceous and cellulose perisperms.

Oleaginous perisperms actively dissolve by themselves. But farinaceous and cellulose perisperms have to be dissolved by the action of a diastatic ferment produced by the epidermal cells of the embryo.

F. J. L.

Winter-colouring of Non-deciduous Leaves. By G. HABERLANDT (*Chem. Centr.*, 1876, 357).—The changes of colour in the non-deciduous leaves depend upon three distinct physiological processes. The yellow colour is due to the decomposition, by light, of chlorophyll existing after its reproduction has ceased.

The brown colour is produced by the formation of a brown-yellow colouring matter from the chlorophyll. Its immediate cause is the cold; the light merely creating the substances which, upon the appearance of frost, act upon and modify the chlorophyll. The subsequent greening of brown twigs must depend upon the mere disappearance of this colouring matter, into which undoubtedly only a small part of the chlorophyll had been changed.

The red colour is traceable to the presence of anthocyan. It sometimes depends on light, at other times not, and generally follows the commencement of rest in vegetation.

Transition-tints depend upon combinations of these colours.

F. J. L.

Xanthophyll. By R. SACHSSE (*Chem. Centr.*, 1876, 599).—According to G. Kraus, an alcoholic solution of chlorophyll, when shaken with benzene, is split up into two colouring matters, the one being dissolved in the benzene, the other, termed by him xanthophyll, remaining in the alcoholic solution, each of these solutions giving a distinct spectrum. Pringsheim contested this statement, and believed that the spectrum of the so-called xanthophyll was merely that of ordinary chlorophyll in very dilute solution. This opinion was founded upon the persistence of the band I in the spectra.

These experiments have been repeated with the same results as those obtained by Pringsheim, but upon substituting "light benzin" from petroleum (sp. gr. ·714) for the benzene, two solutions were obtained giving distinct spectra, the band I being absent from the benzene solution. The yellow colouring matter thus isolated possesses all the characteristics of xanthophyll. F. J. L.

Absorption of Water and Lime Salts by Leaves. By J. BÖHM (*Chem. Centr.*, 1876, 808).—Fresh experiments are detailed, proving that plants absorb water and lime salts through their leaves.

M. M. P. M.

Absorption and Emission of Gas by the Roots of Plants. By P. DEHÉRAIN and G. VESQUE (*Compt. rend.*, lxxxiv, 959—961).—The conclusions drawn by the authors from their experiments are: 1. The presence of oxygen in the soil containing the roots is necessary for the existence of the plant. 2. The root connected with the stem evolves a quantity of carbonic acid less than the oxygen absorbed. 3. Carbonic acid appears not to be derived from the soil, and does not pass to the leaves, in order to build up proximate principles by its decomposition into carbon and oxygen. W. R.

Exchanges of Gas between Plants and the Atmosphere. Reply to a Criticism of Barthélemy. By A. MERGET (*Compt. rend.*, lxxxiv, 957—959).—In this reply the author states that the plants on which he experimented were alive, and that he did not examine the atmospheric gases, as he had reserved them for further experiment. His research does not bear out Barthélemy's theory of cuticular dialysis. W. R.

Combination of Tannin with Vegetable Tissue. By A. MÜNTZ (*Compt. rend.*, lxxxiv, 955—957).—Tannin is absorbed by dead vegetable matter in the same way as it is absorbed by the skin of mammals to form leather. Various fungi, *Penicillium glaucum*, *Agaricus campestris*, &c., when left in contact with tannin in presence of a little chloroform, to destroy life, absorbed a considerable quantity of tannin and were converted into a substance somewhat resembling leather. If they were left alive, no absorption took place, but the tannin was decomposed into gallic acid and glucose. Even higher vegetable tissue has the power of uniting with tannin. W. R.

Tannin in Gentian Root. By H. HAGER (*Chem. Centr.*, 1876, 823).—Some kinds of gentian root contain tannin, others do not: hence the discrepancies in the statements of the books.

M. M. P. M.

Experiments with Barley. By HÄSSELBARTH (*Chem. Centr.*, 1876, 821).—The whole of the nitrogen supplied was absorbed, and the total yield of dry substance was the same when the nitrogen was supplied as calcium nitrate or as ammonium nitrate in soil free from marl. In marl soil the nitrogen was wholly absorbed when supplied as ammonium sulphate or chloride. When these latter salts were applied to unmarled soils, only half of the total nitrogen was absorbed. The worst results were obtained by using acid ammonium phosphate; in marled soil only $\frac{3}{5}$ of the nitrogen was absorbed, and $\frac{1}{2}$ of dry substance was produced; in unmarled soil, $\frac{1}{7}$ of the nitrogen was absorbed and $\frac{1}{20}$ of dry substance produced. It appears as if barley can absorb nitrogen only when presented as a nitrate, or under conditions which permit of ready transformation into a nitrite. M. M. P. M.

Ash of Xanthium Spinosum. By R. GODEFFROY (*Arch. Pharm.* [3], x, 297—302).—This plant is without smell and taste, and although it does not show any signs of an active principle, it has nevertheless been used by pharmaceutists as a remedy for cholera or as a substitute for quinine. The author's investigations seem to show that the plant is quite free from any alkaloïd, glucoside or bitter principle, but that it contains very minute quantities of an ethereal greenish oil similar in taste and smell to chamomile oil. Owing to the small amount of herbs operated upon, it was impossible to examine this oil chemically. The ash, which was rich in potash, amounted to 21·5—24 p. c. It was free from nitre. Its aqueous solution contained CO_2, H_2SO_4, Cl, CaO, MgO, K_2O, and traces of Na_2O. The insoluble portion treated with hydrochloric acid evolved CO_2, and contained H_3PO_4, CaO, MgO, Fe_2O_3, and traces of Al_2O_3. The residue insoluble in hydrochloric acid consisted of SiO_2. Obtained on analysis:—

	SiO_2.	P_2O_5.	H_2SO_4.	CO_2.	Cl.	CaO.	MgO.
(I.)	19·18	6·04	1·68	16·44	2·89	13·56	4·42
(II.)	19·73	5·99	1·72	16·50	2·81	13·48	4·44

	Fe_2O_3.	Al_2O_3.	K_2O.	Na_2O.
(I.)	15·81	traces	19·81	traces
(II.) ..	15·77	traces	19·65	traces

D. B.

Diastatic Ferments. By J. MUNK (*Chem. Centr.*, 1876, 822).—The ferments of saliva and of pancreatic juice are regarded by the author as distinct from those of muscle, stomach, and intestines, inasmuch as the action of the former is strongly developed in acid and in alkaline liquids (within certain limits of acidity and alkalinity), while that of the latter is apparent only in neutral liquids.

M. M. P. M.

Supposed Action of Hops as a Ferment. By L. PASTEUR (*Chem. Centr.*, 1876, 647).—Two portions of dough were set to ferment at a temperature of 25°, one with, and the other without a decoction of hops, prepared according to Sacc's directions. The dough containing the hops did not rise for 10 hours after that without hops. After 36 hours both were equally raised, very little beer-ferment was observable, but small thread-like organisms, some of which moved about. The dough made with hops had a bitter taste, which was approved of by some who tasted it. There is, therefore, no fermenting action in hops; the only result is to give the bread a peculiar bitter taste.

W. R.

Analytical Chemistry.

Huber's Reagent. (*Chem. Centr.*, 1876, 789).—This reagent consists of a mixture of ammonium molybdate and potassium ferrocyanide solutions. It gives a brown colour with the smallest traces of free mineral acids, sulphuric, hydrochloric, nitric, phosphoric, arsenic, sulphurous, phosphorous, but not with arsenious or boric acid, when these are present alone, or accompanied by alkaline salts or alkaline earth salts.

M. M. P. M.

A new Qualitative Reaction for Boric Acid. By M. W. ILES (*Chem. News*, xxxv, 204—206).—On dipping a borax bead into glycerin and gently heating it in the flame, the mass takes fire, burning first with a yellow, then with a deep green flame. With datolite, which contains no soda, the green flame was also visible, but the result was not as satisfactory as anticipated. In subsequent experiments the author, however, found that it was best first to calcine the mineral powder, and moisten with sulphuric acid, heat to expel the acid, then moisten the mass with glycerin and allow it to take fire. Thinking that the carbon exerted some action upon the borate, finely divided charcoal and a borax bead were tried, but they gave negative results. Glycerin and carbonate of sodium bead gave simply a yellow flame. Various metallic bases in a sodium carbonate bead and glycerin also gave negative results with regard to flame. A bead of phosphorus salt and glycerin gave the light green phosphoric acid flame, but of less intensity than that noticed when a potassium chlorate match is burned. A large number of borates were experimented upon in order to test the general applicability of this reaction, and in every case conclusive reactions were obtained, and in a number of borates the glycerin test for boric acid seemed far more delicate than any of the known methods for the detection of this acid.

After comparing his new test with the various tests in existence, the author concludes with an opinion on the chemistry of this reaction. Boron being known to form with alcohol or boric ethers volatile compounds which burn with a green flame, and glycerin being a true triatomic alcohol, the following experiment was undertaken:—about 2 grams of pure crystallised boric acid and 7 c.c. glycerin (94 p. c.) were heated in a small beaker until the boric acid was all dissolved; the liquid was then introduced into a small glass retort and heated gently. A clear limpid liquid soon condensed on the upper side of the retort. This distillate when examined had a sweetish, mildly acid taste, gave a distinctly acid reaction to blue litmus, and showed a faint tinge of green when burned. As the operation proceeds, the liquid in the retort becomes slightly turbid, soon darkening in colour to a reddish-brown, the distillate assuming the same tint. The second portion of the distillate had a pungent taste and an odour of acrolein, showed an acid reaction, and when heated on platinum foil burned with a beautiful green flame. This compound is undoubtedly, therefore, a boric ether, the composition of which has not yet been determined. D. B.

Estimation of Phosphoric Acid in Presence of Silicic Acid. By R. W. ATKINSON (*Chem. News*, xxxv, 127).—Jenkins (*J. pr. Chem.* [2], xiii, 237—239, and this Journal, 1876, ii, 115) mentions that silicic acid does not interfere with the results obtained, and need not, therefore, be removed before adding the molybdate. The author made some estimations of phosphoric acid by this process in presence of different weights of silicic acid, and also in its absence, and found that the silica ought to be completely removed before estimating the phosphoric acid, otherwise the results will be unsatisfactory.

D. B.

Volumetric Analyses of a Mixture of the Sulphates of the Alkalis and Alkaline Earths. By F. JEAN and H. PELLET (*Bull. Soc. Chim.* [2], xxvii, 201—203).—The mixture may consist of sulphates of potassium, sodium, calcium, and magnesium, together with chlorides and nitrates of the same metals, and the amount of sulphuric acid combined with them respectively, is easily determined by proceeding as follows:—

1. *Sulphuric Acid combined with the Alkalis.* The substance to be analysed is dissolved in water, or, if necessary, in hydrochloric acid and neutralised by dilute potash or soda solution. A certain volume of this solution is treated first with a slight excess of baryta-water, then with carbonic acid water, and boiled in order to expel all the carbonic acid gas, and ensure the complete separation of the barium carbonate formed. The amount of normal sulphuric acid required to neutralise the filtrate from the barium carbonate precipitate, is exactly equal to the amount of sulphuric acid previously combined with the alkalis.

2. *Sulphuric Acid combined with Calcium.*—Alcohol is added to the solution containing calcium sulphate, causing its precipitation; the latter is filtered off, washed with dilute alcohol, and boiled with a known volume of normal sodium carbonate solution. The calcium

carbonate resulting from this treatment is filtered off, and the amount of undecomposed sodium carbonate determined by means of normal sulphuric acid. The difference between the total amount of the sodium carbonate solution taken originally, and the residual sodium carbonate, gives the amount of that salt which has been converted into sulphate, and from this the amount of calcium sulphate present in the solution is easily calculated.

3. *Sulphuric Acid combined with Magnesium* is determined in another portion of the solution by the process No. 2, both magnesium and calcium carbonates being precipitated. The sulphuric acid combined with magnesium is obtained by deducting that combined with calcium (previously ascertained) from the sulphuric acid found combined with calcium and magnesium.

4. *Estimation of total Sulphuric Acid (free and combined) contained in Mixtures of Salt.*—The solution under examination is boiled with a known volume of normal sodium carbonate solution, the calcium and magnesium carbonates filtered off, and the filtrate exactly neutralised with normal sulphuric acid, and treated as in No. 1. Results accurate.

5. The authors assayed iron pyrites by the method No. 1, after fusing the sample with a mixture of sodium carbonate and potassium nitrate and sodium chloride, but the results were not accurate. C. A. B.

Volumetric Estimation of Chromium. By F. JEAN and H. PELLET (*Bull. Soc. Chim.* [2], xxvii, 200—205).—The theory of the process adopted by the authors is briefly as follows:—

1. If a neutral solution of an alkaline chromate be treated with baryta-water, an insoluble precipitate of barium chromate is formed, and the alkali which was previously combined with the chromic acid is set free.

2. If the excess of barium in the above solution be precipitated by carbonic acid, the solution boiled, and the barium carbonate filtered off, the filtrate contains all the alkali in the state of carbonate which was previously combined with the chromic acid.

3. From the titration of the alkaline filtrate mentioned above, with normal sulphuric acid, the corresponding amount of chromic acid is obtained.

The Process.—One gram of finely-powdered, levigated chrome iron ore is heated to redness with from 12 to 15 grams of pure fused sodium carbonate for 20 minutes (if the mineral be properly pulverised, the decomposition should be complete, but a second fusion will be necessary if undecomposed chrome-iron be present). The fused mass is exhausted by boiling with water, the ferric oxide filtered off, the filtrate concentrated to about 400 c.c., hydrochloric acid carefully added until there is only a slight alkaline reaction, and the whole refiltered (if necessary) and diluted so as to measure 500 c.c. Of this solution 250 c.c. are exactly neutralised with a few drops of dilute hydrochloric acid, and 50 c.c. of pure baryta-water added, then some carbonic acid water, and the whole boiled for a quarter of an hour in order to expel the excess of carbonic acid. When the solution is cold, it is diluted with water until it again measures 500 c.c., filtered, and 250 c.c. of the clear filtrate titrated with a standard sulphuric acid containing 12·58 grams of SO_4H_2. 100 c.c. of this acid are equivalent to 0·25 gram CrO_4H_2, and the number of cubic centimeters used corresponds exactly with the percentage of chromate of potassium which the chrome-iron would furnish.

The following coefficients may be used with advantage in the calculations :—

$$Cr_2O_3 + 2·545 = K_2O.CrO_3$$
$$K_2O.CrO_3 + 0·3928 = Cr_2O_3.$$

The following precautions must be taken.

1. The sodium carbonate and hydrochloric acid used must be free from sulphuric acid, phosphoric acid, and calcium salts.

2. If a turbidity be observed on the addition of the standard sulphuric acid, the assay must be recommenced, as the carbonate of barium has not been completely precipitated on account of insufficient boiling.

3. The baryta-water must be free from potash or soda, or at all events the amounts of these alkalis present must be accurately determined and deducted from the total alkali found.

The above process is applicable to the assay of insoluble chromates, which are decomposed by fusion with alkaline carbonates.

C. A. B.

Alkalimetric Estimation of Magnesia and of Phosphoric and Arsenic Acids. By F. Stolba (*Chem. Centr.*, 1866, 727—8).—The precipitated magnesium-ammonium phosphate or arsenate is washed with ammonia; the ammonia is entirely removed by washing with alcohol; the precipitate is suspended in water, to which a little carmine tincture is added; and standard acid—hydrochloric, nitric, or sulphuric—is run in from a burette, until a permanent acid reaction manifests itself:

$$Mg(NH_4)PO_4 + 2HCl = (NH_4)H_2PO_4 + MgCl_2.$$
$$Mg(NH_4)AsO_4) + 2HCl = (NH_4)H_2AsO_4 + MgCl_2.$$

1 c.c. normal acid = 20 mgm. MgO; 35·5 mgm. P_2O_5; or 57·5 mgm. As_2O_5. $\frac{1}{10}$th normal acid is preferable to normal.

If it be desired to titrate dried precipitates, they should be suspended in hot water; an excess (measured) of acid run in; and the liquid again rendered neutral by addition of standard alkali.

In order to hasten precipitation of the magnesian phosphate or arsenate, the author recommends continued stirring with a glass rod; the subsequent titration must then be carried out in the vessel used for precipitation, and the same rod must be employed.

The presence of calcium oxalate does not interfere with the titration.

M. M. P. M.

Volumetric Estimation of Aluminium Sulphate and of Alums. By G. Merz (*Chem. Centr.*, 1876, 151).—Sulphate of alumina is treated at the boiling point with a titrated soda-solution, until a very slight but constant alkaline reaction is produced, which may be recognised best when corallin is used as indicator. By this treatment sulphate of alumina is deprived of $\frac{23}{24}$ of its contents of acid, so that the precipitate formed contains for 1 atom of sulphuric acid 8 atoms of alumina. D. B.

Blowpipe Examination of Chloride, Bromide, and Iodide of Silver by means of Bismuth Sulphide. By V. GOLDSCHMIDT (*Chem. Centr.*, 1876, 297).—The author mentions that when chloride and bromide of silver are fused together with bisulphate of potassium, the resulting bead cannot always be considered as a trustworthy test for distinguishing these salts, and that the flame-reaction with copper oxide also separates merely the iodide of silver from the others. The test for bismuth with iodide of potassium and sulphur on charcoal or in a glass tube, was applied inversely to iodine, when it was proved that bromine and chlorine could be distinguished in presence of the former. The following is the test which the author used:—Scoop a cavity in the flat surface of the charcoal, place in it the silver compound, with some powdered sulphide of bismuth, and apply a blowpipe flame (the sulphide is the best reagent, and is easily prepared by fusing bismuth with flowers of sulphur). Iodide of silver gives a bright red, bromide of silver a deep yellow, and the chloride a white incrustation. These incrustations are very volatile, and are formed some distance off the cavity of the charcoal, while near the cavity a white incrustation of oxide and sulphate of bismuth is formed. Similar results are obtained when the mixture is heated in a glass tube open at both ends.

D. B.

Hauer's Method for Disintegrating Lepidolite. By F. STOLBA (*Chem. Centr.*, 1876, 732).—The author's modification of Hauer's process consists in making the powdered mineral into cakes (15 cm. long, 12 cm. broad, and 4 cm. thick) with gypsum and a little water, drying these, and heating them for two hours to semi-fusion. The cakes are then pulverised, and the lithium, cæsium, rubidium, and potassium sulphates are extracted with water. M. M. P. M.

Quantitative Analysis of Slags, Fireclay, Bricks, and Iron Ores. By S. KERN (*Chem. News*, xxxv, 203).—3 grams of the powdered substance (in case of iron ores 1 gram) intimately mixed with 5 grams of dry sodium carbonate, are ignited in a platinum crucible for 1 to 2 hours. The mass is dissolved in aqua regia, and evaporated to dryness. The residue is redissolved in hydrochloric acid, and 20 to 25 c.c. of water added; the resulting precipitate of silica is filtered off, dried, ignited, and weighed. The filtrate is evaporated to 150 c.c., and neutralised at the ordinary temperature with carbonate of sodium, till a reddish-brown precipitate is formed; the solution is next clarified by a few drops of hydrochloric acid, and the iron thrown down by 30 to 40 c.c. of acetate of sodium. The solution is heated on a sand-bath for 10 to 15 minutes, and filtered through a double filter 8 inches in diameter. The precipitate is well washed, and placed in a porcelain dish with the double filter, while the filtrate (A) is set aside. The filter is taken out of the dish after having been well washed. The liquid is heated and the iron redissolved in hydrochloric acid, filtered, and neutralised by sodium hydroxide. The solution is heated for half an hour to 80—90°, in a silver dish containing 5 grams of potassium hydroxide dissolved in 20 c.c. of water, 100 to 120 c.c. of water is next added, and the solution (B) is filtered. The hydrated oxide of iron is redissolved on the filter by hydrochloric acid, and reprecipitated by ammonia. It is then dried, ignited, and weighed as Fe_2O_3. The filtrate B is slightly acidulated with hydrochloric acid, and evaporated to 80 to 100 c.c., and the aluminium is thrown down by an excess of carbonate of ammonium. The liquid is heated until all ammonia gas is expelled, and the precipitate collected on a filter, washed, dried, and ignited. The weight gave Al_2O_3. The filtrate A is evaporated to 100 c.c., and from the liquor heated to 40° the manganese is precipitated by 8 to 10 drops of bromine in the form of hydrated manganese dioxide. It is filtered, dried, ignited, and weighed as manganoso-manganic oxide. The remaining filtrate from the manganese is mixed with 20 c.c. of hydrochloric acid, and evaporated to 80 c.c. The liquor is cooled by adding 40 c.c. of water, and 20 c.c. of oxalic acid is next added. Ammonia is added to the solution, and the mixture left in a warm place for 10 hours. The precipitate, consisting of $CaC_2O_4 + H_2O$, is carefully collected on a filter, strongly ignited, and weighed very quickly as CaO. The remaining filtrate is heated gently, and 200 c.c. of concentrated aqueous solution of disodic phosphate ($HNa_2PO_4 + H_2O$) and 30 c.c. of ammonia is added. The solution is mixed carefully, and left for 12 to 15 hours in a warm place. The resulting precipitate of $MgNH_4PO_4 + 6H_2O$ is filtered, washed, dried, and ignited, till a constant weight is obtained. The residue is $Mg_2P_2O_7$, containing 36·04 p. c. Mg. The process is very successful in the analysis of various products of metallurgical operations. It is easy of manipulation, and quick in execution.

D. B.

Analysis of Chrome-iron and Steel. By W. GALBRAITH (*Chem. News*, xxxv, 151).—1 gram of the chrome-iron is dissolved in dilute sulphuric acid (about 6 pts. of H_2O to 1 of acid). Sufficient permanganate of potassium to oxidise all the iron is now added, and then about as much more, and the solution boiled until the permanganate colour is destroyed. The black or dark brown precipitate, consisting probably of a mixture of permanganate and oxide of manganese, is now filtered, washed well with hot water, and to the filtrate is added a known weight of ferrous sulphate, or better, ammonio-ferrous sulphate, and the excess of iron determined with a standard solution of potassium bichromate. Steels are analysed in precisely the same manner, with the exception that 2 or 3 grams of the sample are taken. By this method very accurate results for the estimation of chromium are obtained. The author estimates the carbon in the irons by the sulphate of copper process. While in the case of chrome irons the iron easily replaces the copper, it is noteworthy that it fails to do so in the case of chrome steels, the steel being only coated with copper, and remaining so for weeks. Probably Weyl's galvanic process gives the best results for chrome steels. The silica, sulphur, phosphorus,

&c., can all be determined as usual in the steel. Their determination in chrome irons is reserved for a future communication. D. B.

Action of Organic Acids on Minerals. By H. CARRINGTON BOLTON (*Chem. News*, xxxv, 114); also by B. J. GROSJEAN (*ibid.*, 190). Bolton finds that, contrary to preconceived ideas based on general notions of the weakness of organic acids, many minerals in fine powder are decomposed by boiling with solutions of citric, tartaric, oxalic, and other organic acids. A large number of carbonates dissolve with effervescence in solutions of the above-mentioned acids, and many sulphides, silicates and other classes of minerals are more or less completely decomposed. The reactions which accompany these decompositions, such as evolution of gases, formation of crystalline precipitates, &c., are characteristic of certain minerals. Moreover, since citric and tartaric acids decompose nitrate of potassium, with liberation of nitric acid, a powerful means of attacking sulphides and arsenides which resist organic acids alone is obtained. Metallic copper, lead, tin, and silver also dissolve in the above mixture of reagents. Chlorate of potassium is slower in action than the nitrate. Various silicates yield readily to the action of citric acid in solution, gelatinising as with mineral acids. Besides these acids, Bolton also examined the action of malic, formic, and acetic acids on carbonates, for the sake of comparison, acetic acid giving the least satisfactory result. For mineralogical as well as microscopic work, the use of these non-volatile acids is recommended, as the dry acids are readily transported, can be dissolved when needed, so that possible injury to the metallic mountings of travelling blowpipe cases is avoided.

The observations of Grosjean on the same subject seem to prove that a weak solution of tartaric acid acts better than a strong solution *of the same weight of acid* upon carbonate of calcium. Another important point in his experiments is that carbonate of calcium, when treated with a large excess of tartaric acid dissolves at once on boiling the mixture. In conclusion he states that Bolton's idea of discriminating minerals by the way they behave with organic acids, might be still further extended to the use of acids of various strengths, and in different degrees of excess. D. B.

Estimation of Oxalic Acid and Oxalates. By F. JEAN and H. PELLET (*Bull. Soc. Chim.* [2], xxvii, 204).—The solution containing either free oxalic acid or oxalates is carefully neutralised with normal soda solution, baryta-water added, and the liquid filtered. The filtrate is then treated with carbonic acid water, boiled, the barium carbonate filtered off, and the filtrate from this is titrated with normal sulphuric acid. The barium oxalate formed must be filtered off before adding the carbonic acid water, otherwise the latter would decompose it and vitiate the results. Results very accurate. C. A. B.

Reactions of an Aqueous Solution of Trimethylamine upon Metallic Solutions. By CAMILLE VINCENT (*Bull. Soc. Chim.* [2], xxvii, 194—196).—The aqueous solution of trimethylamine can easily be obtained on a large scale by the destructive distillation of the residue from the distillation of beet-root molasses (vinasse), the ammonia simultaneously produced being easily removed. The general behaviour of trimethylamine to metallic solutions differs somewhat from that of ammonia. The following results were obtained:—

Reactions with Magnesium Salts.—Magnesium salts are precipitated by trimethylamine from a neutral solution, the precipitate being hydrated oxide of magnesium; an excess of the reagent not dissolving the precipitate. When the solution is acid, no precipitation takes place, but a precipitate is produced on adding to it a solution of sodium phosphate.

Glucinum Salts.—White precipitates, insoluble in an excess of the reagent.

Aluminium Salts.—Gelatinous aluminia is precipitated, soluble in an excess of the reagent.

Zirconium Salts.—White precipitates, insoluble in an excess of the reagent.

Cerous Salts.—White precipitates, insoluble in an excess of the reagent.

Ceroso-ceric Salts.—Reddish-white precipitates, insoluble in an excess of the reagent.

Ferrous Salts.—Dirty-white precipitates, insoluble in an excess of the reagent.

Ferric Salts.—Brown precipitates of hydrated ferric oxide, insoluble in an excess of the reagent.

Chromic Salts.—Green-grey precipitates with the green salts, and bluish-green precipitates with the violet salts, both insoluble in an excess of the reagent.

Manganous Salts.—White precipitate of manganous oxide, which deepens in colour on exposure to the air, but does not dissolve in an excess of the reagent.

Cobalt Salts.—Bluish-grey precipitates, insoluble in excess of the reagent.

Nickel Salts.—Apple-green precipitates, insoluble in excess of the reagent.

Uranic Salts.—Yellow precipitates, insoluble in excess of the reagent.

Zinc Salts.—White precipitates, insoluble in excess of the reagent.

Cadmium Salts.—White precipitates insoluble in excess.

Stannous Salts.—White precipitates insoluble in excess.

Stannic Salts.—White precipitates, soluble in excess.

Antimonious Salts.—White precipitates, insoluble in excess of the reagent.

Antimonic Salts.—White precipitates, soluble in a great excess of the reagent.

Bismuth Salts.—White precipitates, insoluble in excess.

Lead Salts.—A solution of neutral acetate of lead is not precipitated, but the other soluble salts furnish white precipitates insoluble in an excess of the reagent.

Cuprous Salts.—Bright-blue precipitates, insoluble in excess.

Mercurous Salts.—Black precipitates, „ „

Mercuric Salts.—Yellow precipitates, „ „

but changing eventually to a very pale yellow.

Silver Salts.—Dark-grey precipitates, soluble in a large excess of the reagent, with the exception of silver chloride.

Palladium Salts.—Brown precipitates, soluble in an excess of the reagent.

Gold Salts.—Bright-yellow precipitate, with auric chloride, soluble in excess of the reagent.

Platinum Salts.—Platinic chloride produces with trimethylamine a yellow precipitate of the double chloride, which is soluble in a large excess of water (particularly if the latter be hot), and crystallises out on cooling. C. A. B.

Relative Sensitiveness of Phenol and Salicylic Acid Reactions. By A. Almén (*Arch. Pharm.* [3], x, 44—57).—The phenol (carbolic acid) used in these experiments was Calvert's *acidum phenylicum*, I, which proved to be very pure.

1. *Phenol Reaction with Ferric Chloride.*—A dilute solution of phenol gives a fine violet colour when treated with ferric chloride. This colour is lasting if the acid is pure. 1 pt. of crystallised salt was dissolved in 19 pts. of water. One or two drops, or still less, when this solution was further diluted, were added to a solution of phenol, 20 c.c. of which were put into a test-tube. A large excess of ferric chloride, or the addition of hydrochloric acid or ammonia, hinders the reaction, and is liable to destroy the colour. With regard to the sensitiveness of the reaction, it may be mentioned that an indication of a violet colour is obtained with a solution containing 1 pt. of phenol in 3,000 pts. of water.

2. *Phenol Reaction with Ammonia and Sodium hypochlorite.*—By warming an ammoniacal solution of phenol with sodium hypochlorite, a deep-blue colour is obtained which is lasting, but turns red on the addition of acids. Alkalis restore its blue colour. The colour is destroyed if chlorine is liberated by the addition of acids, more especially if the solution is hot. If much phenol is present, for instance, as much as $\frac{1}{1000}$, the quantity of ammonia and hypochlorite of sodium may vary considerably without injuring the reaction. With very dilute solutions, however, a deficiency of ammonia is more injurious than excess, whilst excess of sodium hypochlorite destroys the reaction. With very weak solutions, it is best to use about 10 drops of 10 per cent. NH_3 solution.

With regard to the sensitiveness, Salkowski mentions that a distinct blue coloration is obtained with a solution containing $\frac{1}{4000}$, using chloride of lime and ammonia. According to the author's method, the presence of phenol in a $\frac{1}{5000}$ solution could be detected very easily when 20 c.c. of the solution are used. With dilutions to $\frac{1}{10000}$ to $\frac{1}{15000}$, blue colours were produced after a short time; whilst, with $\frac{1}{20000}$ to $\frac{1}{30000}$, a change could be perceived only after boiling the mixture for 15 minutes. A solution of $\frac{1}{40000}$ to $\frac{1}{50000}$ phenol, gave a reaction after 24 hours. No reaction could be obtained with $\frac{1}{60000}$. A moderately concentrated solution of sodium hypochlorite was used in these experiments, which was prepared from chloride of lime, by triturating the latter with water, filtering, precipitating with sodium carbonate, and again filtering. 3—5 drops of this solution were used in every experiment.

3. *Phenol Reaction with Aniline and Sodium Hypochlorite.*—Jacquemin mentions (*Revue méd. de l'Est*, 1874, 10, 359), a reaction for phenol depending on its conversion into sodium erythrophenate. By treating phenol with an equal weight of aniline and adding sodium hypochlorite, a pure dark-blue and constant colour is obtained, which acids redden and alkalis turn blue. The reaction is said to be very sensitive and unalterable by various organic substances, such as alcohol, fat, &c. But it is also stated that aniline alone, without the addition of phenol, produces a blue colour with sodium hypochlorite, and that with dilute solutions, the latter gives violet liquids, which, after a short time, assume a dirty-yellow colour, and finally become colourless. In mixtures it is, therefore, difficult to distinguish the aniline colour from the phenol colour, especially if moderately concentrated solutions of phenol are worked with. But, by using a small quantity of sodium hypochlorite, both phenol and aniline assume the same colour in weak solutions. The bluish-violet colour produced may last for $\frac{1}{2}$ to 2 hours, and may then disappear, leaving the dirty-yellow colour for 24 hours longer. An excess of sodium hypochlorite interferes with the reactions. 30—40 c.c. of phenol solution were used, and indications obtained with dilutions of $\frac{1}{50000}$ to $\frac{1}{60000}$ after the lapse of 5—24 hours.

4. *Phenol Reaction with Bromine-water.*—Landolt has shown that an excess of bromine-water gives a crystalline precipitate of *tribromophenol* in concentrated or dilute solutions of phenol, and Fresenius mentions that slight precipitates of this substance are soluble in alkalis without being reprecipitated by hydrochloric acid. A distinct turbidity is said to be formed with solutions containing $\frac{1}{44000}$ to $\frac{1}{55000}$ phenol. After a few hours, a crystalline precipitation is produced with a $\frac{1}{57000}$ phenol solution. In repeating these experiments, the author treated 20 c.c. of the dilute phenol solution with concentrated bromine water, until the mixture assumed a reddish-yellow constant colour of bromine. To this mixture, 5,000, 10,000, and 20,000 parts of distilled water were added, when a milky turbidity was produced, which, in a few minutes, deposited a white-yellow, crystalline, shining precipitate. A slight precipitate was obtained after 24 hours, when a solution containing $\frac{1}{60000}$ phenol was treated under similar conditions. Under the microscope, this precipitate could be identified as forming fine stellated needles of *tribromophenol.* The reaction is not only very sensitive and simple in application, but it has also the advantage that the consistency and the quantity of the precipitate may, with some practice, serve as an approximate indication of the phenol contents.

5. *Phenol Reaction with Mercurous Nitrate and traces of Nitrous Acid.*—Plugge mentions (*Zeitschr. f. Analyt. Chem.*, xi, 173), that carbolic acid gives a deep red colour with mercurous nitrate and a minute quantity of nitrous acid. The author obtained, with solutions containing $\frac{1}{5000}$, a red colour; with $\frac{1}{10000}$, a yellowish-red colour; while with $\frac{1}{15000}$ and $\frac{1}{20000}$ solutions, uncertain reactions were obtained. Although, according to Plugge's account, a distinct colour is obtained

with solutions containing $\frac{1}{60000}$ phenol, while solutions containing $\frac{1}{200000}$ phenol give a coloration which is perceptible, the author could not obtain a more delicate reaction than that by which a solution contained $\frac{1}{15000}$ of phenol, in spite of his having prepared the nitrate in the pure state, and free from any oxide.

6. *Phenol Reaction with Mercuric Nitrate and traces of Nitrous Acid.*—This reaction proved to be an exceedingly delicate one. It was used, like Meyer Hoffmann's reaction for tyrosine, viz., boiling the phenol solution with a neutral solution of mercuric nitrate (as used for titrating urine), and adding a very dilute solution of fuming nitric acid or nitrite of potassium, drop by drop. 20 c.c. of phenol solution was used, and gave with $\frac{1}{5000}$ phenol, a slight precipitate with a fine red colour. Solutions of 1 pt. phenol and 5,000, 20,000, and 30,000 pts. of water, gave fine red liquids. With $\frac{1}{40000}$ to $\frac{1}{60000}$ solutions, at first faint colours were formed, which, in 5 minutes, assumed fine light-red colours. 1 pt. of phenol, with 150,000 and 200,000 water, gave a reaction with nitrite of potassium, but not with nitrogen tetroxide.

7. *Phenol Reaction with Millon's Reagent.*—This reaction, which was found out accidentally by the author, forms the most sensitive of all phenol reactions. Millon's reagent is prepared by dissolving mercury in ordinary fuming nitric acid, boiling and diluting the solution with 2 vols. of water. 20 c.c. of phenol solution is boiled with 5—10 drops of Millon's reagent, and to the hot solution nitric acid is added, drop by drop, until the precipitate formed is re-dissolved. The mixture now assumes a fine red colour, which remains constant for several days. A large excess of nitric acid should be avoided if good results are to be obtained. The sensitiveness of the reaction is so great, that a solution of $\frac{1}{2000000}$ phenol still gives a faint colour, so that about $\frac{1}{100}$ of a milligram, or $\frac{6}{1000}$ of a grain of phenol could be detected. It is well known that other substances give similar reactions with Millon's reagent. But this circumstance, connected with the question as to the best means of applying the reagent for phenol alone, cannot be dealt with in the subject of the present investigation.

Salicylic Acid Reactions.—1 gram of the best salicylic acid of commerce—so-called sublimed salicylic acid, consisting of pure white and small fine shining crystalline needles, with but little smell—was dissolved in hot water, and the solution made up to 1 litre. By further dilution with distilled water, solutions of given strength were prepared, and 20 c.c. used in each trial. The phenol reactions which were the most sensitive, viz., 1, 2, 4, and 7, gave the following results when applied in the same manner to salicylic acid:—

Reaction (2) always gave unsatisfactory results; blue or green colours could not be obtained at a concentration of 1 part of salicylic acid to 1,000 pts. of water.

Reaction (4) answers as well as with phenol; the crystals formed had the same characteristic properties when investigated microscopically. The only perceptible difference was that the reaction was not quite so sensitive, $\frac{1}{40000}$ and $\frac{1}{50000}$ giving neither precipitates nor microscopic crystals.

Reaction (7) gave the same red colour at a dilution of 1 part of salicylic acid with one million parts of water.

Reaction (1) gave much better results, the sensitiveness being so great, that immediately after the addition of ferric chloride and shaking, a deep violet colour is produced with solutions containing $\frac{1}{100000}$ of salicylic acid, or even $\frac{1}{800000}$ or $\frac{1}{1000000}$. This reaction is, therefore, as sensitive for salicylic acid as that of Millon's reagent for phenol, and is very suitable for distinguishing phenol and salicylic acid if present in dilute solutions.

In a further communication, the author intends to deal with the practical uses attached to these reactions. D. B.

Contributions to the Chemical Knowledge of Cacao. By PIERS TROGANOWSKY (*Arch. Pharm.* [3], x, 32—37).—1. Preparation of *Theobromine.* A weighed quantity of powdered cacao is treated with petroleum-ether to remove fat; the residue is mixed with an equal weight of the original cacao-powder; magnesia and water are added, and the mixture dried at 60—70°. The dried mass is powdered very finely and boiled in a flask with 80 p. c. alcohol, repeating the boiling a second time; the mixture filtered whilst hot; the filtrate evaporated on a water-bath; and the residue treated with petroleum-ether and washed on a filter with alcohol, until the theobromine loses its brownish colour and becomes colourless. The quantity of alcohol used for washing is measured, and from this the quantity of theobromine dissolved is calculated and added to that left on the filter. The author undertook a large number of analyses by this method, the results of which seemed to show that the amounts of theobromine do not always correspond with the quality and value of the samples of cacao.

2. *Cacao-fat.* A weighed quantity of cacao is extracted with petroleum-ether and the residue left on evaporation is weighed. It is shown that the fatty matter is fairly the same with all kinds of cacao, so that it cannot be used for distinguishing various qualities. The author condemns Björklund's method of treating cacao with ether, in order to ascertain whether the fatty constituents in cacao consist of cacao-fat or of animal fat.

3. *Starch.* The cacao, after exhaustion with petroleum-ether and 80 p. c. alcohol, is treated with 6 p. c. alcoholic potash-ley and digested for 24 hours. After this it is first washed with alcohol, then with distilled water, until the washings are colourless; and the residue is boiled with sulphuric acid until all the starch has disappeared. The sugar produced is then estimated, and from the latter the quantity of starch calculated. The amount of starch in cacao does not vary sufficiently to be used as a means of distinguishing between various qualities. In chocolate, however, the quantity of starch should not exceed 7 p. c. (after deducting the amount of sugar).

By treating cacao exhausted with petroleum ether with alcohol, the author obtains various coloured tinctures whose behaviour to reagents he uses for distinguishing various substances contained therein. Since the presence of alcohol very often hinders the reactions, aqueous extracts were prepared. The following are the results obtained:—

The first few drops of sulphuric acid produce a change of colour in the liquid: see II.

I. The first drops of acid produce no change: Carracas, Puerto Cabello, Surinam.

1. To another portion of the solution add cupric sulphate:

a. The liquid assumes a bluer colour, with turbidity, and turns green when boiled, depositing blue flakes: Carracas.

b. The liquid assumes a green colour, and yields a blue precipitate turning brown on boiling: Puerto Cabello, Surinam.

2. Another portion is treated with nitric acid:

a. No reaction: Surinam.

b. Violent reaction, assuming yellow colour: Puerto Cabello.

II. The liquid assumes a raspberry-red colour after the addition of the first drops of acid, but turns brown and lastly black when the whole of the acid is added.

1. Nitrate of silver is added:

a. White precipitation: Para, Guayaquil, Trinidad.

b. Greyish-violet precipitate: the liquid in which the precipitate is suspended is:

α. Colourless: Domingo.

β. Reddish: Bahia.

c. Blue-violet flakes in pink solution: Martinique.

2. Another portion of the solution is treated with neutral acetate of lead:

a. Light brown flakes, reddish liquid: Para.

b. White flakes, liquid colourless: Guayaquil, Trinidad.

3. Treated with stannous chloride: pink precipitate, pink liquid:

a. Turning lighter when boiled: Guayaquil.

b. Turning violet when boiled: Trinidad.

4. *Albuminates.* Several analyses proved that the contents of albuminate are of but little importance in estimating cacao.

5. *Ash.* The percentages of ash are nearly the same in all kinds; but the husks are richer in ashes than the cotyledons. In chocolate the quantity of ash should not be higher than 4 p. c.; otherwise an adulteration with cacao-husks may have taken place. D. B.

Examination of Wax. (*Chem. Centr.*, 1876, 151).—The correct specific gravity of wax, 0·960 to 0·963, excludes a large number of adulterations which would otherwise be made, and of which that with resin is especially worthy of notice. The fact that adulterations with resin are not altogether unfrequent, was proved some time back when in Berlin several chemists and also druggists were supplied with wax containing 20 p. c. of resin. As the determination of the specific gravity of wax is a tedious operation, it is often neglected. The examination with "Liq. ammon. caust." is, however, very easily undertaken, and depends only upon the fact that pure wax floats on the surface of this liquor, whereas resinous wax sinks to the bottom.

D. B.

Testing of Castor Oil. By H. HAGER (*Chem. Centr.*, 1876, 389).—Pure castor oil when mixed with 5 volumes of spirits of wine of 90 per cent. strength gives a clear solution, whereas if any fatty oil be present even 10—20 times the volume of spirit will fail to do so.

To estimate the amount of admixed fat, shake at a temperature of 30°, a portion of the oil with twice its volume of 90 per cent. alcohol. Upon cooling, and when at rest, it will separate into three layers, the lowest of which is generally the foreign oil. This gives a tolerably accurate determination of the quantity of admixed oil. F. J. L.

Estimation of Hydrocyanic Acid in the Dead Body. By N. Sokoloff (*Chem. Centr.*, 1876, 603).—The various parts of the suspected body are digested with water strongly acidified with sulphuric acid, and then the whole is subjected to distillation over a water-bath for 2 or 3 days, the water being replenished from time to time.

The longer the distillation is carried on, the greater the accuracy of the result. The quantity of hydrocyanic acid is estimated by titration with silver nitrate, any sulphuretted hydrogen that may have been formed being first removed by lead acetate. The muscles are to be carefully examined, as they contain the poison more especially.

F. J. L.

Some New Reactions for Alkaloïds. By R. Godeffroy (*Arch. Pharm.* [3], ix, 434—440).—The difficulty with which alkaloïds, especially if present in small quantities, are detected in chemico-legal investigations, is well known—in fact, no ready method of separation has yet been discovered, so that all communications regarding new reactions for alkaloïds are desirable.

Basing his researches on the peculiarity of the fact, that most of the known reagents for alkaloïds also produce characteristic precipitates in solutions of alkaline metallic salts (especially salts of caesium and rubidium), the author was led to investigate whether the chlorides of the so-called heavy metals are equally suitable for the formation of difficultly soluble double salts with the alkaloïds. The following results were obtained:

I. A solution of ferric chloride in hydrochloric acid gives yellowish-red precipitates in hydrochloric acid solutions of the following alkaloïds: aconitine, piperine, strychnine and veratrine.

In the case of atropine, quinine and cinchonine, the precipitate formed is soluble in an excess of the precipitant; brucine, caffeine and morphine are not precipitated.

The precipitate produced by ferric chloride and the alkaloïd consists of a double ferric chloride, and the hydrochloride of the alkaloïd. One molecule of the double salt contains 1 mol. of ferric chloride and 2 mol. of the chloride of the alkaloïd. This double salt is readily soluble in water and dilute hydrochloric acid.

By treating an aqueous solution of quinine hydrochloride with an aqueous solution of ferric chloride and evaporating the mixture, avoiding the separation of a basic iron salt by adding a sufficiency of hydrochloric acid, small yellowish-red crystals of the double chloride are obtained, exhibiting the form of monoclinic prisms ∞ P with ∞ ₽ ∞, oP and subordinate ∞ ₽n. The angle 0P : ∞ ₽ ∞ is only slightly greater than 90°, so that the crystals approach very near to the rhombic system. Analysis of the crystals led to the formula $Fe_2Cl_6.2(C_{20}H_{24}N_2.O_2.2HCl)$. They are readily soluble in water and alcohol, possess a bitter ink-like taste, and can be heated to 100—120° without being altered.

II. A solution of antimony trichloride in hydrochloric acid produces a precipitate in hydrochloric acid solutions of the following alkaloïds: aconitine, quinine, cinchonine, conine, piperine, strychnine, veratine. Atropine, nicotine and solanine are precipitated only from very concentrated solutions, while caffeine and morphine are not precipitated. These precipitates are flocculent and white (the piperine precipitate is yellow), and dissolve readily in dilute hydrochloric acid. Their solutions are decomposed by the addition of water, separating oxychloride of antimony.

For the quinine-precipitate the formula $SbCl_3.C_{20}H_{24}N_2O_2.2HCl$, was obtained. This salt when dried in the air forms a white amorphous powder, not soluble in water without decomposition. It dissolves very easily in dilute hydrochloric acid, less easily in concentrated acid. When heated to 80° it melts and yields on cooling a hard, brittle yellowish-white mass, which may be easily crushed to a fine white powder.

III. A solution of stannous chloride forms precipitates in hydrochloric acid solutions of the following alkaloïds: aconitine, atropine, brucine, quinine, cinchonine, codeine, conine, morphine, piperine, solanine, strychnine and veratrine. These precipitates are crystalline, white and massive. Nocotine is precipitated only from concentrated solutions, and caffeine is not at all precipitated.

The above precipitates produced by stannous chloride are not readily soluble in water, especially in presence of hydrochloric acid; the morphine and quinine salts being the least soluble. The formula, $SnCl_2.C_{17}H_{19}NO_3.HCl$ was obtained for the morphine salt.

By evaporating a solution of caffeine in hydrochloric acid with a solution of stannous chloride, crystals of a double salt are obtained having the following composition: $SnCl_2.C_8H_{10}N_4O_2.HCl$. At first sight these crystals appear in the form of simple rhombohedrons. However, by further investigation, it will be seen that of the three pairs of faces only two pairs are physically unique and have equal plane angles, while the third pair varies in physical properties and plane angles. The crystals show therefore the monoclinic combination, ∞ P.0P.

IV. Laubenheimer obtained precipitates in very dilute solutions of quinine salts by the addition of an aqueous solution of *silico-tungstic acid*, and as this chemist did not investigate this reaction more closely, the author resolved upon extending it for other alkaloïds, and obtained results which proved that this acid forms the most sensitive reagent for alkaloïds. The sensitiveness of this reaction was specially tested in the case of the hydrochlorides of quinine, cinchonine and atropine.

An aqueous solution of quinine hydrochloride gave a distinct precipitate with a few drops of an aqueous solution of silico-tungstic acid even if the solution contains only 0·004 p. c. of the alkaloïd. When 0·002 p. c. was present, a turbidity was still perceptible.

A solution of cinchonine hydrochloride was still rendered turbid by silico-tungstic acid, when only 0·0005 p. c. or $\frac{1}{200000}$ of the alkaloïd was present, while a hydrochloric solution of atropine gave a turbidity when only 0·0065 p. c. or $\frac{1}{15385}$ of the alkaloïd was present.

These precipitates therefore undoubtedly form the most sensitive reactions for alkaloïds. They are more or less difficultly soluble in concentrated hydrochloric acid, are decomposed by caustic alkalis, with separation of the alkaloïd and formation of silico-tungstate of the alkali-metal. With ammonia they give at first clear solutions, which are afterwards rendered turbid by the separation of silicic acid. By fusing the precipitates a mixture of silicic acid and tungstic acid is obtained which is insoluble in water, concentrated hydrochloric acid and ammonia.

According to Marignac, silico-tungstic acid does not yield difficultly soluble or insoluble compounds with metallic salts, so that this reaction for alkaloïds is not effected thereby. D. B.

Estimation of Veratrine and Physostigmine. By E. MASING (*Arch. Pharm.* [3], ix, 310—317).—The author finds that Mayer's process for estimating alkaloïds by titration with potassic-mercuric iodide, is applicable to the determination of the two alkaloïds named above, in pharmacopœial preparations, provided that the substance under examination is not a mixture of a great many alkaloïds. The titration should be carried out in a very slightly acidulated solution: the double iodide which is thrown down is more soluble in acidulated than in pure water. The solution is made by dissolving 13·546 gram mercuric iodide, and 49·8 gram potassic iodide in 1000 cb.c. of water: 1 cb.c. of this solution precipitates $\frac{1}{20000}$ of an equiv. of veratrine ($C_{32}H_{52}N_2O_8 = 592$) = 0·0296 gram. As the solubility of the double iodide produced amounts to 1 in 14570, 0·068 milligrm. must be added to the amount of veratrine found, for each cb.c. of liquid present when the titration is complete. The final point of the reaction is determined by placing two small quantities of the liquid, filtered from the precipitate, in cylinders side by side, and adding to one a drop of a solution containing mercury; the production of a slight turbidity, readily noticed by comparing the contents of the two cylinders, shows that a sufficiency of the precipitating solution has been added.

Sabadilline. From the results of titration with the potassio-mercuric-iodide solution, the author is inclined to regard Couerbe's formula for sabadilline, viz., $C_{20}H_{26}N_2O_5 = 374$, as more probable than Weigelin's, viz., $C_{41}H_{66}N_2O_{13} = 794$. 1 cb.c. of the titration liquid = 0·0374 gram sabadilline. The solubility of the mercur-iodide of sabadilline is 1 in 17630 of pure water, and 1 in 19300 of water containing 1 per cent. of sulphuric acid. The correction to be made for each cb.c. of liquid in the volumetric determination amounts to 0·05 milligrm.

Sabatrine. Weigelin's formula, viz., $C_{51}H_{86}N_2O_{17} = 998$, is regarded as probably correct. The solubility of the double iodide in water, or in water containing 1 per cent. sulphuric acid is 1 in 2450: the correction to be made in the determination amounts to 0·408 milligrm. for each cb.c. of liquid.

Physostigmine.—Hesse's formula, viz., $C_{15}H_{21}N_3O_2 = 275$, agrees with the author's results.

The potassio-mercuric iodide solution serves to determine 1 part in 9500 of pure water, or 1 part in 8800 of water containing 1 per cent. of sulphuric acid. The double iodide is soluble in 1300 parts of boiling water. The correction for each cb.c. of liquid in the process of estimation amounts to 0·105 milligrm. M. M. P. M.

Estimation of Conine. By N. Sokoloff (*Chem Centr.*, 1876, 604).—The conine having been separated in the usual manner, may be estimated by titration with dilute sulphuric acid, turmeric paper being used as indicator. F. J. L.

Estimation of Albumin in Urine. By A. Bornhardt (*Chem. Centr.*, 1876, 604).—The albumin, after being well washed, is transferred to a specific gravity bottle, and the weight taken. The weight of albumin is then found by the formula $x = \frac{d. 1\cdot314}{0\cdot314}$, where d is the difference between the weight of the bottle when filled with water alone, and when filled with water and the albumin.

F. J. L.

Studies on the Colouring Matter of Wine, and on Wine-colouring. By O. Griessmayer (*Dingl. polyt. J.*, cxxiii, 531—536).—The following investigations were undertaken:—

1. Blue "Bozen grapes" with small berries, were deprived of their husks, and the latter digested with water in which carbonic acid gas was introduced for five minutes. After the lapse of 18 hours the red liquid was decanted, and the residue washed until the washings were colourless and neutral. The residue was digested with 92 p. c. alcohol for 24 hours, and gave a deep red liquid, which was decanted. The greater part of the alcohol was removed by distillation, and the residual liquid evaporated on a water-bath, leaving a dark red mass soluble in cold water. The husks, which had been exhausted with alcohol, were in the next place washed with water till the washings were colourless, and then treated with 92 p. c. alcohol, when a reddish-violet solution was obtained (2nd alcoholic extract). A third treatment with alcohol resulted in the formation of a pale red liquid. After the latter had been removed by washing, the husks were digested with dilute sulphuric acid for 18 hours. They assumed a darkish-red colour; their solution, however, was almost colourless.

(1.) *Properties of the first Aqueous, slightly Acid, and Pink Extract.*—*a.* Acetic, tartaric, or dilute sulphuric acid turns it red. Ammonia changes this red into bluish-violet. Neutral tartrate of potassium does not alter the extract. *b.* Ammonia or soda turns it greenish-brown; tartaric acid turns the brown colour red. *c.* Sulphate of ammonium and alum: no change. *d.* Tannin: no change. *e.* Acetate of lead gives a precipitate, which is turned blue on the addition of acetic acid, and turns red if an excess of the latter is added.

(2.) *Properties of the first Alcoholic Purple Extract.*—*a.* Tartaric acid turns it to a blood-red colour. *b.* Ammonia gives a bluish-violet colour, turned red by tartaric acid or sulphuric acid. This red colour is rendered greenish-brown by soda, partly green and partly violet by ammonia. *c.* Soda: green, then brown. *d.* Neutral tartrate of potassium: bluish-violet. *e.* Alum: bluish tinge; after the addition of tartaric acid, red. *f.* Acetate of lead: blue precipitate. Fehling's liquid is reduced by both these extracts.

(3.) *Properties of the second Alcoholic Reddish-Violet Extract.*—*a.* Soda: dark green. After adding sulphuric acid the green turns red, while the red is turned dark green by soda, or grey-violet green by ammonia. *b.* Ammonia: pale green. *c.* Acetate of lead: green colour (no precipitate), which turns blue-violet after the addition of acetic acid, but not red.

2. Berries of bluish-red "Malaga grapes" were treated in a similar manner, their husks being in the first place digested for 18 hours with carbonated water. A second extract was made, which yielded a colourless liquid. After decanting this extract, the husks were treated with 92 p. c. alcohol, when a yellow extract with bluish tinge was formed.

(1.) *Properties of the first slightly Aqueous Reddish Extract.*—*a.* Ammonia: green. *b.* Soda: greenish-yellow. *c.* Acids: red. *a* and *b* reddened by acids.

(2.) *Properties of the second Aqueous Colourless Extract.*—*a.* Soda: greenish-yellow. *b.* Ammonia: green. *c.* Sulphuric acid: red, the red turning blue with ammonia. *d.* No reaction with acetate of lead.

(3.) *Properties of the Alcoholic Yellow Extract.*—*a.* Soda: dark greenish-yellow. *b.* Ammonia: light greenish-yellow, assuming a fine red colour after the addition of sulphuric acid, the red being changed to a blue-violet by ammonia. *c.* Acids redden it. *d.* Acetate of lead: yellow opalescence, not turning blue, but red, after adding acetic acid.

3. In order to recognize artificial wine colouring, the following colouring matters were investigated with regard to their behaviour to reagents. The reactions are given in the following table (p. 370):—

With reference to the previous results, the following four qualities of wine were analysed. The second wine, "Desse Pauillac," was investigated more closely, in order to ascertain the presence of roseine, which, however, could not be found.

1. "Bordeaux," from a private cellar, origin not stated. 300 c.c. were evaporated, and the residue taken up with water. Ammonia formed a greenish-brown coloration and darkish-brown precipitate. Soda: greenish-brown, then dark brownish-yellow coloration, and finally a precipitate. Sulphuric acid: red. Ferric chloride: dark brown coloration. Tannic acid, acetate of lead: blue precipitate. Baryta: blackish-grey precipitate.

2. "Desse Pauillac," 1869, of Péros Mandis et Fils et Cie., Bordeaux. It was not evaporated. Zinc and hydrochloric acid: gradual and slight discoloration. Soda and ammonia: blackish-brown. Acetate of lead: dark violet precipitate. Evaporated and then treated with acetate of lead: greyish-blue precipitate. Baryta: brownish-black precipitate. Ferric chloride: black. Tannic acid, cupric sul-

Reagents.	Bilberry.	Elderberry.	Danewortberry.	Mallow Flowers.		Beetroot.	Cochineal.	Brazil-wood.	Roseine.
	Vaccinium Myrtillus.	*Sambucus niger.*	*Sambucus ebulus.*	*Flores Malvæ arboreæ.*	*Flores Malvæ sylvestris.*				
Zinc and hydrochloric acid	Gradually discoloured	Discoloured	Brownish red	Red	Red	Decolourised	Brownish red to orange	Red, then decolorised	Quickly decolorised
Ammonia ...	Greenish brown	Greenish black	Greenish black	Brown yellow	Brownish yellow	Dirty pale reddish brown	Dark purple red to blue violet	Blood red	Ditto
Nitric acid...	Blood red when cold, orange red when boiled	Red; yellow when boiled	Red; yellow on boiling	Blood red; yellow on boiling	Red; on boiling yellow	Decolorised in the cold	Pale yellow in the cold; yellow on boiling	Red; yellow on boiling	No reaction in the cold; orange to dark red on boiling
Baryta......	—	Greyish green precipitate; liquid colourless	Greyish green precipitate; liquid greenish	Green precipitate; green liquid	Greenish yellow precipitate; yellow liquid	Precipitate grey; liquid colourless	Purple precipitate; red liquid	Dirty brownish red	—
Soda	Greenish brown	Reddish brown; greenish yellow when diluted	Like the former (elderberry)	Green precipitate	Brownish yellow	Pale greyish brown	Dark purple with violet tinge	Red	—
Acetate of lead	Blue precipitate	Greyish green precipitate; liquid yellow	Ditto	Bluish violet precipitate; violet liquid	Grass green precipitate; yellow liquid	Flocculent brown precipitate; colourless liquid	Blue violet precipitate	Flesh coloured precipitate	—
Cupric sulphate	Violet	Dark brown red liquid	Ditto	Blue precipitate; bluish violet liquid	Dark brown precipitate; dirty green liquid	Green liquid; slight precipitate in suspension	Bluish violet liquid	Different colours	—
Sodic carbonate	Bluish black	Dark greyish green	Brownish green	Dark olive green	Light olive green	Blackish red	Purple red	Blood red	—
Borax	Purple	Red	Red	Dark brownish green	Green	Red	Blood red	Ruby red	—

phate: no reaction. 50 c.c. were next evaporated to dryness, the residue being taken up with ammonia and shaken with ether. A colourless liquid was obtained, which remained colourless after adding acetic acid. (If roseine had been present a red colour would have resulted.) 100 c.c. of the original wine were shaken with 15 grams of powdered binoxide of manganese (method according to Lamattina, 1876, 222, 375), and the yellowish liquid filtered. The residue was treated with 92 p. c. alcohol, and the alcoholic liquid treated with concentrated acetic acid, and a few drops of ammonia added. It remained colourless (roseine would assume a red colour).

3. "Vino nero di Spalato," from Leibenfrost and Co., Vienna. This wine has a blackish-red colour, and was diluted with three times its bulk of water. Nitric acid gave, even after two minutes' boiling, no change. Zinc and hydrochloric acid only paler after long boiling.

Ammonia: black. Soda: black. Carbonate of sodium: black. Borax: blackish-violet. Cupric sulphate: no change. Baryta: blackish-grey. Acetate of lead: greyish-blue precipitate.

4. "Red Vöslau," from Leibenfrost and Co., Vienna. Nitric acid: no change when cold; quickly rendered colourless on boiling. Zinc and hydrochloric acid: gradually paler. Ammonia: black. Soda: black. Carbonate of sodium: black; brown when diluted. Borax: blackish-red. Cupric sulphate: no change. Ferric chloride: black. Baryta: greyish-black. Acetate of lead: light greyish-blue.

From these results the author concludes that all the wines investigated were pure and not coloured. D. B.

Detection of the Principal Colouring Matters used in the Adulteration of Wine.—By G. Chancel (*Compt. rend.*, lxxxiv, 348—351).—For purposes of wine adulteration the following substances are generally used: fuchsine and the various preparations termed caramels, ammoniacal cochineal, sulphindigotic acid, logwood, and the lichen reds.

All these bodies are precipitated by basic acetate of lead; fuchsine, however, if present in considerable quantity, is only partially precipitated; the remainder, which colours the filtrate rose, may be separated by agitation with amyl alcohol.

The lead precipitate is treated with a dilute solution of potassium carbonate (2 grams to 100 of water); the cochineal and sulphindigotic acid are thus dissolved out together with the fuchsine contained in the precipitate. From this liquor the fuchsine is separated by neutralisation with acetic acid and agitation with amyl alcohol. The rose-coloured liquid thus obtained is identified as a solution of fuchsine by means of the spectroscope.

The solution now containing the potassic salts of carminamic and sulphindigotic acid is treated with a drop of sulphuric acid, and again shaken with amyl alcohol. The carminamic acid is now dissolved out, and may easily be identified by means of the spectroscope; three dark bands are seen, one between the lines D and E, the second in the green, and the third, less marked, in the blue.

The indigo now left alone in the solution is detected by the blue colour and the absorption-band seen between C and D.

That part of the original lead precipitate which was insoluble in potassium carbonate is now treated with a 2 per cent. solution of potassium sulphide, which dissolves the colouring matters of the logwood and of the wine itself. The logwood colouring matter may be thus extracted, but it is simpler to test for it directly in the wine by addition of calcium carbonate and two or three drops of lime-water; the filtered liquid is almost colourless in the case of a natural wine, but is of a fine red colour if logwood is present.

The lichen red is detected by washing the insoluble portion left after treatment with potassium sulphide and dissolving it in alcohol; a red colour and a definite absorption-band then reveal its presence.

F. D. B.

Adulteration of Wine. By H. W. VOGEL (*Deut. Chem. Ges. Ber.*, ix, 1906—1911).—Some of the commoner substances used to colour wine are rosaniline, bilberries, cherries, mallows, and, in the neighbourhood of Meissen, the berries of the *Ligustrum vulgare* (privet). The author, whilst allowing the value of the tests hitherto proposed for the detection of these bodies, considers the spectroscope an indespensable help. The results of his investigations could hardly be explained without reproduction of the wood cuts.

G. T. A.

Examination of Beer. By F. A. HAARSTICK (*Chem. Centr.*, 1876, 201).—The use of grape-sugar in a sugar-refinery led to an investigation of various samples of grape-sugar obtained from the International Agricultural Exhibition at Barmen in 1874.

To determine the total quantity of non-saccharine bodies, Hoppe-Seyler's polarisation apparatus was used. A sugar-solution containing about 8 per cent. showed, however, 12·5 p. c. on the scale, and as the greater portion of these samples behaved in a similar manner, it was thought very probable that they contained a body possessing great rotatory power. This body proved to be Bechamp's amylin, which was separated in the following way:—The dilute solution of white grape-sugar was allowed to ferment at 20° with washed head-yeast, and on the second and third day a small quantity of fresh yeast was added. The filtered solution showed on the fourth day 4·1 p. c.; as however the sugar had undergone complete fermentation, the solution was evaporated, and from its concentrated form the amylin was precipitated by 95 vol. p. c. alcohol. The separated mass, after repeated washing with alcohol, was a white amorphous substance, melting at 90°. At this stage it has a rotatory power of 125, as given by Béchamp, but after drying it at 100°, the rotatory power rises to 168. To Böttger's bismuth test and Fehling's copper solution, it behaves like grape-sugar; 10 c.c. of copper solution require 0·170 grm. amylin for reduction.

As this body resists the fermentation with yeast, the author thought it advisable to use this property as a means of detecting the presence of grape-sugar in beers, in which malt had been partially replaced by this surrogate. One litre of beer was therefore evaporated on a water-bath, until the residue when cold assumed a thin syrupy state; to this liquid alcohol of 90 p. c. was added drop by drop from a burette, with constant agitation, until a volume of about 300 c.c. had been used; and the separation of dextrin was completed with 95 p. c. alcohol, until the filtrate did not show the least turbidity when mixed with an equal bulk of 95 p. c. alcohol. The mixture was then left at rest for 12 hours, filtered, and the greater part of the alcohol distilled off. The remainder was evaporated to dryness on a water-bath; the solid dissolved in distilled water; the solution diluted to one litre, and left to ferment with yeast at 20°; and after addition of fresh yeast on the second and third day, the fermentation was completed on the fourth day. Beers prepared without grape-sugar gave a solution which showed zero on the scale of the polarisation apparatus, while with beers prepared with grape-sugar the plane of polarisation turned 2·0 to 3·4 to the right, as observed on Hoppe's scale. The amylin in this solution may be separated from the brown liquid after decolorisation with animal charcoal. D. B.

Tests for Malt-Extract. By H. HAGER (*Chem. Centr.*, 635—636). —The tests for the purity of malt-extract are as follows:—

1st. Its peculiar sweet taste and pleasant smell of new bread.

2nd. Its almost clear solution in water; 5 grams of the extract should dissolve in 45 c.c. of distilled water to form a slightly turbid solution which is easily filtered. The insoluble portion examined under the microscope was found to consist of amorphous coagulated matter, ferment particles, and long tetragonal or hexagonal prisms.

3rd. 10 c.c. of a 10 p. c. filtered solution was placed in a test-tube, 1·5 cm. in diameter, and mixed with 10 c.c. of a cold saturated solution of picric acid. In a few minutes it became so turbid as to render the liquid opaque. An adulterated sample did not give this reaction. Half the weight of the precipitate thrown down with the picric acid consists of proteic substances.

4th. 10 c.c. treated with excess of gallic acid, should become quite opaque. An adulterated sample showed only a slight turbidity.

W. R.

Differences observed in Unadulterated Milk. By E. REICHHARDT (*Arch. Pharm.* [3], ix, 440—442).—The specific gravity of cow's milk varies from 1·018 to 1·045, but is generally 1·040. To ascertain the amount of water added to milk, the author recommends the use of the areometer. It is also known that differences are produced by the food given to cows. The milk of different races of cows naturally varies to some extent, as may be seen from the following degrees indicated by the areometer:—

I = 17·5; II = 17·5; III = 18·25; IV = 19·0; V = 18·5.

Nos. I and IV were subjected to an accurate chemical investigation, and gave the following results:—

	I.	IV.	Difference.
Butter fat	3·41	4·02	0·61
Casein..........	2·37	3·92	1·55
Milk-sugar	6·13	6·60	0·47
Water..........	88·09	85·46	—
	100·00	100·00	

In practice this difference is of some importance. By taking one litre of milk, which is equal to 1000 grams, or in reality rather more, viz., 1030 or 1040 grams, we buy with milk IV at least 6·1 grams more butter, 15·5 grams more cheese, and 4·7 grams more milk sugar, so that with a daily consumption of 1 litre, and at the same price, we obtain with milk IV 2226·5 grams more butter, 5657·5 more cheese, and 1715·5 more milk sugar per year than with milk I. D. B.

Method of Detecting and Estimating Castor and other Fixed Oils in Balsam of Copaiba. By DR. MUTER (*Analyst*, i, 160—161).—This oleo-resin, commonly but wrongly termed a balsam, has been said to be subject to admixture with fixed oils, especially castor oil. The methods which have been proposed for examination may be summarised as follows:—(1.) Pure balsam gives a translucent, and not an opaque emulsion, with strong solution of ammonia. (2.) Pure balsam, if boiled with water for some hours, leaves a tenacious resin. (3.) The specific gravity.

The tests are very insufficient, and in observing the close affinity between copaivic and pinic acids, it struck the author that advantage might be taken of the difference of solubility of the soda-soap in certain solvents. The experiments which were undertaken showed that, besides the essential oil (which is dissipated in the process of analysis), good commercial balsam contains only copaivic acid, which forms a sodium salt instantly soluble in the ether-alcohol mixture, and a little altered resin, not so readily saponifiable, forming a salt only slowly soluble. The actual process which the author employs, is as follows:—3 to 4 grams of the sample are weighed in a dry flask and saponified on a water-bath, with 50 c.c. of alcohol and lumps of caustic soda (not less than 5 grams). When all is dissolved, water is added, and the whole washed into a half pint basin and evaporated to 100 c.c. over a low gas flame. Dilute sulphuric acid is then added till the whole just becomes permanently turbid, and then solution of caustic soda is dropped in till it just clears again. By this means a solution is obtained with the least possible excess of alkali, and with a good amount of sodium sulphate. The whole is now evaporated to perfect dryness. The residue is removed to a small wide-mouthed stoppered bottle, treated with 10 c.c. of ether-alcohol, and well shaken up. The liquid is filtered, and the operation repeated with two successive quantities of 10 c.c. The residue in the bottle and on the filter now consists of sodium oleate and sulphate, if the balsam be impure, and of the latter only, if pure, with a little trace of the insoluble resin soap already referred to. The contents of the bottle and filter are then dissolved in warm water, and, after heating until all smell of ether is gone, the whole is boiled, freely acidulated with hydrochloric acid, and set to cool. If, when it is cold, nothing but a few specks of brown resin should rise to the surface, the balsam is pure, but if an oily layer be formed, it is adulterated, and the smell of the separated oleic acid will at once determine whether it is actually castor oil or not. In the case of the presence of oil, 2 grams of pure and dry white wax are added, and the whole heated till the wax melts with the oleic acid. On cooling, a solid cake is formed, which is detached from the side of the beaker, and the fluid below passed through a filter. The cake is once more melted in boiling water, cooled, detached, dried by gentle pressure in blotting paper, put into a water-oven in a weighed platinum dish till dry, then weighed, and the weight of the wax used is deducted. The calculation is then performed as follows:—(1). To the weight in grams found 0·20 is added for loss of oleic acid in the solvent, and then the proportion obtained, viz., 95·100: total oleic acid : x. (2). Calculate to per cent. from the quantity taken, and from the total percentage deduct 6 per cent. for possible altered resin in balsam.

In conclusion, the author mentions that the process, although it looks formidable, is in practice very simple and accurate. D. B.

Technical Chemistry.

Electro-deposition of Cobalt. By R. Böttger (*Chem. Centr.*, 1876, 640).—With two Bunsen's elements, it is possible to deposit in a few minutes a bright coating of cobalt on brass or copper from a solution of the chloride of cobalt and ammonium. The solution is best prepared by dissolving 40 grams of crystallised cobalt chloride, and 20 grams of ammonium chloride in 100 c.c. of distilled water, adding 20 c.c. of ammonia. W. R.

Deposition of Carbon and other Bodies from the Gases of Blast Furnaces. By Pattinson (*Dingl. polyt. J.*, ccxxiii, 473—481).—In blowing out two large furnaces which had been worked for five years, the inner brickwork was found to be completely corroded, so that it was necessary to rebuild the whole of the walls.

The author investigated the corroded portions of these furnaces with the view of ascertaining the cause of this destruction, and the best means of preventing it, and gave a full account of his results in *Engineering*, 1876, xxi, 262. His analyses seemed to show that the corroded bricks were impregnated with a carbonaceous mass, and that the accumulation of this substance in the pores of the bricks resulted in destroying them. The cause of this separation of carbon is easily explained by the behaviour of carbonic oxide to ferric oxide. Bell has shown that at a temperature between 200° and a red heat the carbonic oxide present in the gases from blast-furnaces is converted into carbonic acid, with separation of carbon if the gases are brought in contact with ferric oxide. In the case at present under investigation, all these conditions seem to correspond with Bell's results, and the formation of carbon is therefore sufficiently well explained.

Although the above-mentioned appearances were observed with other furnaces, they were nevertheless absent in many cases, proving that other causes than those already described result in a carbon separation. The differences in height of furnaces influences these appearances, as the gases of blast furnaces are exposed to a greater pressure and can therefore enter the pores of the bricks more readily. Besides this, the various sizes in which the ore is used when placed in the furnaces materially influence the results obtained—smaller lumps of ore, *e.g.*, ore from Northamptonshire, producing a relatively greater pressure of gases. D. B.

Combustibility of Blast-Furnace Gases. By E. BELANI (*Chem. Centr.*, 1876, 729—732).—Blast furnace gases are sometimes found to be very incombustible. The author gives analyses of various gases which show that the percentage amount of nitrogen is about 66 to 68: that of CO varies from 20 to 30; and that of CO_2 from 5 to 15.

The chief cause of incombustibility is however the solid matter contained in the gases from some furnaces, especially from those burning coke. This solid matter is present in a state of extremely fine subdivision, and cannot be entirely removed by passing the gas through water. The solid matter was found to contain SiO_2, CaO, MgO, Al_2O_3, K_4FeCy_6, Fe_2O_3, S, NH_3, CO_2, &c. M. M. P. M.

Manganese Steel. By GAUTIER (*Chem. Centr.* 1876, 735).—The properties of a steel containing 0·38 p. c. of carbon, 1·38 p. c. of manganese, and 98·24 p. c. of iron are detailed. The steel seems to be above the average quality. For the detailed properties the original must be consulted. The paper also appeared in *The Iron and Coal Trades' Review* for 1876. M. M. P. M.

Phosphorus Bronzes and their Uses. (*Chem. Centr.*, 1876, 635).—From analysis and observation it appears that phosphorus has a double chemical action in bronzes. The oxide of tin is completely reduced, and forms a homogeneous chemical compound, which is more durable than the pure metal. By straining, phosphorus bronze does not become crystalline, and it is almost unattacked by sea-water or dilute hydrochloric acid. One of its best properties is that it is not altered in composition by recasting, and is more easily melted than the usual alloy. Its use increases daily, and it will probably supplant brass, and for some purposes even iron and steel. W. R.

The Refining of Crude Petroleum. By AD. OTT (*Chem. Centr.*, 1876, 704 and 719).—The oil is fractionated; the escaping gases when condensed by pressure form liquids named *rhigolin*, *cymogen*, *kerosolene* or *petroleum-ether*, and *sherwood oil.* They are used in the manufacture of ice. The next product is collected till it has a density of 65° to 59° B. This product, named "crude naphtha," is redistilled and separated into *gasolin* (sp. gr. 95—80° B.), *naphtha* (80—65° B.), and *benzin* or *ligroïn* (80—65° B.). From 100 parts of crude oil 1½ part of gasolin, 10 parts of naphtha, and 4 parts of benzin are obtained. The next fraction is from 65° or 58° B. to 38° B., or till the colour becomes yellow. It forms 55 p. c. of the crude oil, and is used for illuminating purposes. The last distillate yields paraffin; its specific gravity is 38° to 25° B., and it forms 19 p. c. of the crude oil, 10 p. c. being carbonised. The oil from which the paraffin has been extracted by freezing, pressing, &c., is used for lubricating after treatment with sulphuric acid and caustic soda.

If the heavy oils are very slowly distilled, no paraffin oil is obtained, for it splits up into light oils. This method is termed technically "the cracking of the oils." The three products are then crude naphtha, illuminating oil, and a residue. The latter may be distilled and worked up for paraffin. The illuminating oil is mixed with 2 p. c. of its volume of sulphuric acid and agitated; a tar subsides as sediment and is separated; it is then agitated with caustic soda to remove acid.

The illuminating oil is unfortunately very frequently adulterated with naphtha, which renders explosions not unfrequent (from the *Scientific American*, 18th May, 1872).

The following table gives a list of the various oils, their specific gravities, and boiling-points.

	Sp. gr.	B.	B. P.
Rhigolin	0·625	—	18° C.
Gasolin	0·665	85°	49
A Naphtha	0·708	70	82
B Naphtha	0·724	67	104
C Naphtha	0·742	65	150
Kerosene (lamp oil) ..	0·804	45	176
Mineral sperm oil	0·847	36	218
Lubricating oil	0·883	29	300
Paraffin	0·848 (?)	—	—

W. R.

On a Process for rendering the Arsenical Residues of the Manufacture of Aniline Colours innocuous. By C. WINKLER (*Chem. Centr.*, 1876, 651—654).—The conversion of aniline into fuchsine is best accomplished by heating it with arsenic acid for 5 to 8 hours to 182°. The residue, after distillation, is treated with boiling water and filtered; common salt is then added, whereby the rosaniline arsenate is converted into hydrochloride, sodium arsenate being formed. The fuchsine crystallises out, leaving sodium arsenate in solution.

The process devised by the author for recovering the arsenic existing in the mother-liquor as sodium arsenate is as follows:—The mother-liquor is exactly neutralised with soda, and the colouring matter which separates is collected and sold as an inferior quality;

excess of soda is then added till the liquid has a strong alkaline reaction. It is then evaporated till a pellicle forms on the surface, and poured over a mixture of limestone and coal dust, 30 kilograms of powdered limestone and 25 kilograms of coal dust being used for every 100 kilograms of a saturated solution of sodium arsenate. The mixture is stirred till it has become solid, owing to the crystallisation of the sodium arsenate. This salt, when heated alone, is non-volatile; with carbon, part of the arsenic is expelled, but in presence of both carbon and lime all the arsenic is volatilised. The mass is heated in a reverberatory furnace provided with two soles, one above the other. The lower one should be heated to moderate redness, while the upper one has a temperature of some hundred degrees. The mixture of sodium arsenate, lime, and coal is placed in charges of 500 kilograms at a time in the upper sole to dry. The partition between the two portions of the furnace is then opened, and the dry mixture allowed to fall on to the lower sole. The air must then be nearly excluded, so as not to burn the coal intended to reduce the arsenate. The arsenic may be obtained either as metal or as oxide. If it is wished in the metallic form the vapours are conducted into a large chamber and condensed. It is advisable to have two chambers, to be used alternately. The gas which issues from the chamber, although it contains but a small trace of arsenic, has nevertheless a very disagreeable smell, owing probably to the presence of compounds resembling cacodyl, and should be led into a furnace and burned, to convert the arsenic into arsenious oxide, which, as it is present in so small a quantity, has no smell. If coke be substituted for coal, this disagreeable smell is to a large extent avoided.

If it is desired to recover the arsenic as arsenious oxide, air must be allowed to come in contact with the vapour on its exit from the muffle. The arsenic burns, and the arsenious oxide is condensed in flues of the usual construction.

By this process 2,500 kilograms may be worked in 24 hours, equal to 800 kilograms of arsenic acid.

The residue consists of calcium and sodium carbonates. It is lixiviated with water, and filtered by the systematic method of filtration adopted in the soda manufacture, and the strong soda-solution is used to neutralise a fresh quantity of fuchsine mother-liquor. The limestone may be dried and used again, but it is advisable to throw it away after some time, as it becomes full of coal-ash. The recovery of 800 kilos. of white arsenic costs £1 2*s.* 6*d.*, while its market price is about £10. This process has been adopted in many works, and has proved very successful. W. R.

Dyeing with Aloes. By V. Preston (*Chem. Centr.*, 1876, 390).—The colouring matter from aloes may be obtained by digesting 10 kilos. of the resin in 60 kilos. of nitric acid. After a strong disengagement of gas, the golden-yellow liquid is evaporated, first over a sand-bath, and then over the water-bath, and finally water is added. This precipitates the colouring matter, which, however, requires purification with water before it can be dried. In this manner about 66½ per cent.

of pure colouring matter is obtained, which is completely soluble in water, alcohol, or ether.

With this substance and its combinations, wool and silk have been most successfully dyed, the colouring matter being used in a variety of ways, and the colours obtained being most varied and well fixed.

F. J. L.

Fining of Wines. By A. v. BABO (*Chem. Centr.*, 1876, 639—649, and 669—670).—The author first describes several methods of filtering wines through paper or sand, with or without pressure. The wine is then purified by the use of isinglass, $3\frac{1}{2}$ decigrams to about 860 litres of wine, whipping it into a froth, and allowing it to settle. Milk, in the proportion of 1 litre of fresh milk, or $1\frac{1}{2}$ litre of blood, or 12 fresh eggs to 150 litres of wine may also be used. Gelatin is also advantageous.

W. R.

Solubility of Silk in an Alkaline Glycerin-copper Solution. By J. LÖWE (*Dingl. polyt. J.*, ccxxii, 274—275).—Schlossberger uses nickel-ammonium oxide, Persoz chloride of zinc, and Spiller concentrated hydrochloric acid, for dissolving silk, while the author recommends the use of an alkaline glycerin-copper solution, which he prepares in the following manner:—16 grams of pure copper sulphate are dissolved in 140 to 160 grams of distilled water, and 8 to 10 grams of pure glycerin of 1·240 sp. gr. added. The mixture is then well shaken, and whilst it is cold, soda-lye is added drop by drop until the light-blue precipitate of hydrated cupric oxide first formed has been dissolved without leaving a residue, and formed an azure-blue liquid, which, it may be added, can be kept without filtration for any length of time and without being decomposed, provided that pure chemicals have been used for its preparation.

Moderately concentrated solutions of this mixture are said to dissolve silk very easily, forming a thick liquid, which, however, can be filtered, although very slowly. The most remarkable character of this solution is, that it does not attack wool, cotton, or linen, even when left in contact for hours, so that it may serve as a ready test for the contamination of silks by other ingredients. But it was found that silks which were dyed black with iron salts were less readily soluble in this solution, the cause of this being that the insoluble ferric oxide present acted as an outside casing, and thus protected the fibre from the powerful action of this solvent. Such silks can be rendered soluble by placing them in a solution of ammonium or potassium sulphide, afterwards washing them, and removing the iron sulphide formed with hydrochloric acid. Silks dyed with other mordants did not show this difficulty.

D. B.

On the Products of the Dry Distillation of the "Vinasse" from Beetroot Molasses. By CAMILLE VINCENT (*Bull. Soc. Chim.* [2], xxvii, 148—154).—Beetroot molasses contains 40—50 p.c. of crystallisable sugar, and is used for the manufacture of alcohol; the residue of this manufacture is called "vinasse;" it is a brown liquid, and forms 4·1 times the weight of the molasses. It is usually evaporated to dryness, and calcined to obtain the salts which it contains; and the gas resulting from its combustion is used for evaporating the more dilute liquor. If submitted to dry distillation, it gives a residue of carbon mixed with alkaline salts, and a distillate from which the author separated ammonium carbonate, hydrosulphide, and cyanide. This liquid was neutralised with sulphuric acid, and partially distilled. The distillate contained free hydrocyanic acid, methyl cyanide and sulphide, and methyl alcohol, the latter in the proportion of 1·4 litre of alcohol to 100 kilos. of molasses. On further distillation, a number of ethers were obtained, and on fractionation and decomposition with baryta, gave formic, acetic, propionic, butyric, valerianic, and caproic acids. Acetic acid was present in largest quantity.

On concentrating the residue of the distillation, ammonium sulphate is deposited; the mother-liquor of this salt refuses to crystallise, but on addition of an alkali, trimethylamine is evolved in large quantity; no other methylamine appears to be formed. The solution of trimethylamine in water gives a dark-grey precipitate with silver salts, difficultly soluble in excess; it does not dissolve silver chloride; it gives a blue precipitate with salts of copper, and does not dissolve the precipitate when added in excess. The precipitate produced as solutions of nickel salts is also insoluble in excess. Aluminium hydrate, however, dissolves. Trimethylamine condenses to a liquid boiling at + 8°. When passed through a red-hot tube with hydrochloric acid gas, it gives methyl chloride and ammonium chloride. Trimethylamine might thus be obtained in large quantity.

The oils which separated from the first ammoniacal distillate contained bases boiling from 110° to 268°. They are as yet not identified. A small quantity of phenol was also obtained; and finally the gas evolved consisted of—

CO_2, 46·18; CO, 11·77; H, 33·90; and C_2H_4. 8·17 per cent.

W. R.

The Waste Material of the Parchment Manufacture as a Source of Oxalic Acid. By C. O. Cech (*Dingl. polyt. J.*, ccxxiv, 70).—The author states that oxalic acid is now manufactured by a Berlin firm from the waste material (which was formerly burned) obtained in the manufacture of parchment. M. M. P. M.

Cochineal-red for Woollen Goods. By A. Kielmeyer (*Dingl. polyt. J.*, ccxxiv, 96).—14 kilos. gum are mixed with 15 litres water, 17·5 kilos. cochineal lake, and 2·25 kilos. fustic are added; the whole is warmed at 60° until dissolved; then 1 kilo. oxalic acid and 1·75 kilos. acid sodium oxalate are added; and after solution, and when the whole has become quite cold, 2·25 kilos. crystallised sodium acetate are thrown in. The goods, after dyeing, are dried at a gentle warmth for one or two days, then steamed under a slight pressure, well dried, washed, and again dried. M. M. P. M.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXI.—*Examination of Substances by the Time Method.*

By J. B. HANNAY, F.R.S.E.

Part I.—*Hydrates.*

IN a former paper* I have pointed out that an examination of the rate at which the volatile constituent of a compound is driven off, may afford us valuable information as to the constitution of the body so examined, and would bring out the relation between the varying vapour-tension of a decomposing body and its chemical constitution; and evidence was adduced in the paper referred to, proving this to be the case. It was intended to extend this method to all kinds of compounds in which there exists a volatile constituent, and as water affords us the most numerous class of such bodies, this field was first to be examined. It was suggested by my friend Dr. Ramsay, that the composition and constitution of many of the amorphous hydrates, such as aluminic and ferric hydrate, whose compositions are somewhat indefinite, might be accurately determined by this method, as the vapour-tensions of hygroscopic and combined water would differ so much that a definite distinction could be made between them. Dr. Ramsay having kindly offered to work up this portion of the subject, the research was divided into two portions, and, as the work is carried on by us in different laboratories, we shall publish from time to time such portions of our work as may form completed sections.

a. *Crystalline Hydrates.*

As the various hydrated sulphates present us with a series of isomorphous water-compounds, I considered that an examination by this method might throw light on their relations; and more especially I hoped to determine whether isomorphous bodies, which are so similar in their statical properties, would show any such similarity in their dynamical deportment. We already know that many bodies which are statically alike, are, dynamically very different; also that a body which has only one statical formula, may show a variety of modes of decomposition—that is, have several dynamical formulæ; so I wished to determine whether the hydrous sulphates which are statically alike would show any relation when viewed from a dynamical point of view. The compounds which seemed likely to throw most light on the subject, were the well-known sulphates having the following crystalline forms:—

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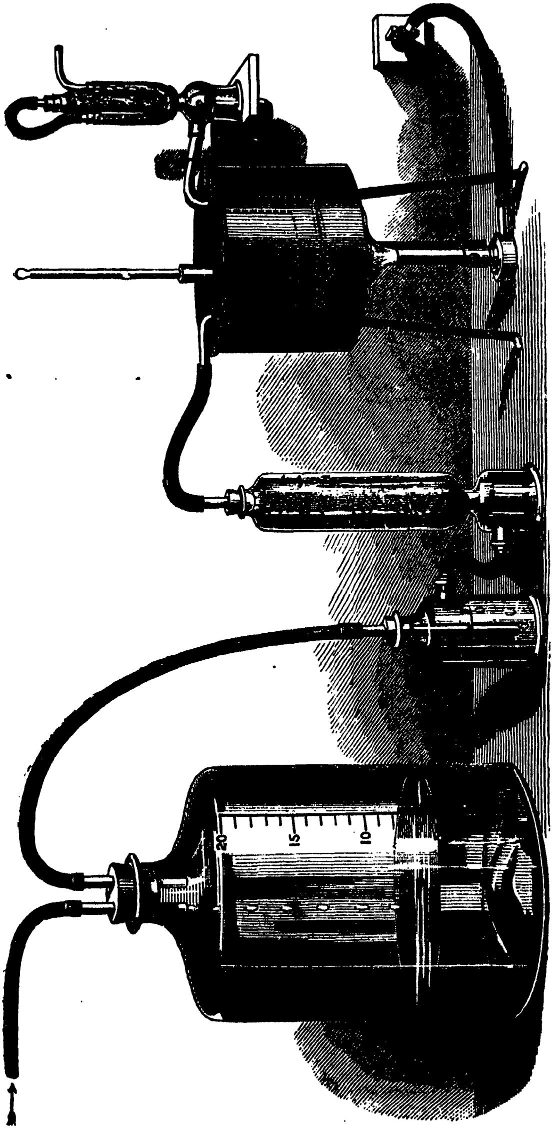
* "Examination of the Hydrous Constituent in Minerals," *Mineralogical Magazine*, 1877, No. 4.

$Na_2SO_4.7H_2O$	trimetric
$MgSO_4.7H_2O$	"
$ZnSO_4.7H_2O$	"
$FeSO_4.7H_2O$	monoclinic
$Na_2SO_4.10H_2O$	"

Of hydrated sulphates of sodium only the above two are known, but of the other sulphates several hydrates with a lower number of water molecules have been formed. Two other hydrates of magnesium sulphate, besides the heptahydrated salt are known, viz., a hexhydrated and a monohydrated salt, the first obtained by crystallising a solution of the salt above 30°, and the other by heating the ordinary sulphate to 150°. The zinc salt, on the other hand, forms four other hydrates besides the heptahydrate, hex-, penta-, di- and mono-hydrates having been formed. The first is formed like the magnesium salt by crystallising above 30°; the second by boiling the ordinary hydrate with alcohol of sp. gr. 0·856; the third by adding strong sulphuric acid to a solution of zinc sulphate in water; and the fourth when the ordinary salt is dried at 100°. It would appear that every compound of ferrous sulphate with water from one molecule up to 7 has been obtained by various means, except the hexhydrate, which occurs in the two isomorphous sulphates of magnesium and zinc. The penta-, tetra-, and di-hydrates may be obtained by abstracting water (by means of oil of vitriol) from the hepta-hydrate, while the trihydrate is obtained by evaporating and crystallising a solution of ferrous sulphate at about 60°, while the mono-hydrate is obtained by heating the heptahydrate for some time a little over 100°; thus we find that there is not very much similarity between the subsidiary compounds of these isomorphous sulphates; we see this on tabulation:—

$FeSO_4.7H_2O$	$Na_2SO_4.7H_2O$	$MgSO_4.7H_2O$	$ZnSO_4.7HO$
—	—	$6H_2O$	$6H_2O$
$5H_2O$	—	—	$5H_2O$
$4H_2O$	—	—	—
$3H_2O$	—	—	—
$2H_2O$	—	—	$2H_2O$
H_2O	—	H_2O	H_2O
$FeSO_4$	Na_2SO_4	$MgSO_4$	$ZnSO_4$.

It is quite likely, however, that some of these compounds may not be real compounds but merely mixtures of others; such, I fear, is the case with some of the iron compounds, as I have been unable to obtain either the tetra- or tri-hydrate in anything like purity.



DEHYDRATION APPARATUS.

Such being the state of our knowledge, I saw that there was plenty of room for work, and I set about a careful examination of the hydrates above mentioned. The apparatus I have found to work best after several trials, is represented in the subjoined sketch, and I would wish, in the first place, to point out its advantages.

I found, in the first place, that I could not aspirate the air through the apparatus, as the india-rubber joints were somewhat porous, and as the air near a boiling water-bath is very moist; this caused the determinations to be rather high. A pressure method was therefore used, as in the figure on page 383, in which it will be seen that there are no india-rubber joints after the air passes over the substance, thus eliminating this leakage error. In the second place, I found that the pumice-stone soaked with vitriol in the little tower had to be renewed after every dehydration; so, to prevent this loss of time, I placed some vitriol in the bottom of the apparatus, and, by causing the moist air to bubble through this, it was only necessary to renew this acid every time—that in the tower suffering very little deterioration. As the substance which is being examined is thus under a pressure (measured by the depth of this vitriol) greater than that of the atmosphere, the tube containing the substance was placed in the boiling water at a depth proportional to the column, so that the temperature was such that the conditions became the same as though the air within the apparatus had the same pressure as the atmosphere.

I found in the course of experiment that a salt which refuses to give up its moisture at 100° in ordinary air, may give it up to air dried over strong sulphuric acid, or, should this prove ineffectual, air dried over phosphoric anhydride may cause its dissolution. It is obvious that the rate of dehydration depends, not only upon the vapour-tension of the water in the substance, but also on the vapour-tension of the water in the air; that is, whenever the tension of aqueous vapour in the atmosphere falls below that of a hydrate, dehydration will take place (the phenomenon of efflorescence in salts), and, where such tension rises above that of any hydrate, hydration will take place, commonly called deliquescence. It is thus seen that to dehydrate substances of very low vapour-tension, the tension of the water-vapour in the air used must be reduced lower. From these considerations we learn that the rate of dehydration is not a measure of the vapour-tension of the water in compounds, but a measure of the difference between such tension and that of the moisture in the air employed; but where this is extremely small compared with that in the salt, the time of dehydration may be considered as a direct measure of the vapour-tension. These relations have not as yet been fully wrought out, and I leave it over till a future communication to give an account of my work in this direction. So much by way of preface. We will

now consider the results obtained by the examination of the above-mentioned salts.

The first salt I examined was the decahydrated sulphate of sodium, and I wished to find whether the vapour-tension would afford us any information about the formation of the heptahydrate. I found that at 100° the salt, when spread in a layer about 1 mm. thick in the tube, parted with the whole of its moisture in about 3·25 minutes, so that it was impossible to obtain separate weighings of the amounts given off in different times; when, however, the temperature was lowered, the moisture came off at a much slower rate, and so rendered an examination of the rate possible. At 60° the weighings gave the following loss per cent.* See also Curve, No. I, Appendix.

Intervals.	Total time.		Loss per cent.
30′	0h	30′	4·80
30	1	0	9·27
60	2	0	18·04
30	2	30	22·82
30	3	0	26·24
60	4	0	34·33
120	6	0	51·89
30	6	30	55·78

It will be seen from these figures that the moisture is given off from this compound at a fixed rate, or at least nearly so, the curve which graphically expresses these results being reduced to a straight line. There is not the slightest change in the rate at the point where the residue equals $Na_2SO_4.7H_2O$, showing either that the compound is not directly formed from the decahydrate, or that its vapour-tension is the same. As the solubility of sodium sulphate decreases above 33°, and as the anhydrous salt is less soluble than the hydrate, it is supposed that at 33° the hydrate begins to be dehydrated in solution, and as this is a kind of critical point in the salt, I made an examination of it at that temperature. The following are the results:—

---

* I do not give all the determinations done or the original figures, but only the calculated percentage, as the paper would be rendered too voluminous were all the figures to be tabulated. The quantities given are therefore often averages of several determinations.

Temperature 33°.

Intervals.	Total time.		Loss per cent.
30′	0h	30′	2·52
30	1	0	5·29
30	1	30	6·94
60	2	30	10·85
30	3	0	12·51
30	3	30	14·61
90	5	0	22·15
60	6	0	26·34
120	8	0	34·31
60	9	0	36·81
60	10	0	40·52
60	11	0	46·27
70	12	10	51·08
60	13	10	52·51
60	14	10	52·93
60	15	10	53·18

These results are shown graphically in Curve No. VIII. They still show us no sign of the heptahydrate, but they do show a sudden falling off in the rate at the loss of about 51 per cent. Now a loss of 50·31 per cent. leaves a compound $NaSO_4.H_2O$, so we see that at 33° the decahydrate does not split up into water and the anhydrous salt, but into water and a monohydrate. It thus appeared that when the temperature was lowered the salt became more complicated, so another determination was done at 10° in order to see if any further complication would ensue. The dehydration went on so slowly in this case that the salt was merely placed in a desiccator and weighed at intervals. Of course, taking the substance out of the desiccator caused moist air to get in, so that the rate was somewhat lower than it would be in the other apparatus, and the results are not quite comparable.

Temperature 10°.

Intervals.	Total time.		Loss per cent.
45′	0h	45′	2·93
135	3	0	8·66
30	3	30	10·78
120	5	30	15·37
60	6	30	17·43
180	9	30	25·36
120	11	30	31·19
60	12	30	33·66
60	13	30	36·43
60	14	30	38·29
60	15	30	40·77
60	16	30	42·30
60	17	30	43·87
60′	18h	30′	45·15
30	19	0	46·09
60	20	0	48·14
60	21	0	50·31
60	22	0	51·32
60	23	0	52·54
120	25	0	55·20
30	25	30	55·65
60	26	30	56·45
60	27	30	56·66
60	28	30	56·67
60	29	30	56·69

These results are graphically represented as Curve No. X. Here we see, as was expected, a further complication has arisen, and another multiple compound appears as the rate becomes slower, about 44 per cent. of loss agreeing with a residue having the formula $Na_2SO_4.2H_2O$. There is not as yet any indication, however, of the heptahydrate in this curve. The observation that the salt becomes more complicated as the temperature is lowered, is quite in keeping with the facts recently discovered by Professor Guthrie, whose cryohydrates are the results of further complications obtained by lowering the temperature; and we know that this is the case with matter generally, whether solid, liquid, or gaseous.

A sample of the heptahydrate was prepared and examined at 33° to find if its behaviour were different from the normal salt. The following are the numbers so obtained:—

Intervals.	Temperature 33°. Total time.		Loss per cent.
30′	0h	30′	2·68
30	1	0	5·44
60	2	0	9·78
60	3	0	13·95
60	4	0	17·85
120	6	0	27·72
60	7	0	33·81
60	8	0	37·32
60	9	0	42·83
60	10	0	45·18
60	11	0	47·99
60	12	0	49·22
60	13	0	50·65
60	14	0	50·93

We see from Curve No. IX, which represents the above table graphically, that the result is almost the same as with the decahydrate. The sulphates of sodium were not examined any further; but I intend at a future time to examine them at lower temperatures, to find whether the complexity increases with the fall of temperature as above indicated. Thus we have of hydrates of sodium sulphate—

Already known	$Na_2SO_4.10H_2O$
"	" 7 "
New	" 2 "
"	" 1 "

The next compound I examined was magnesium sulphate, and I found that at ordinary temperatures it did not lose any moisture in a desiccator over strong sulphuric acid, at least from 10° to 14°. It lost only the small quantity of hygroscopic moisture (about ·3 per cent.) after being two days over acid. The sulphate was therefore examined at 100° C. The following table gives the results. See also Curve No. II.

Temperature 100°.

Intervals.	Total time.		Loss per cent.
5′	0h	5′	8·36
10	0	15	16·68
15	0	30	27·96
15	0	45	30·36
15	1	0	31·18
30	1	30	32·28
30	2	0	32·95
30	2	30	33·73
90	4	0	34·80

This salt had been thoroughly freed from hygroscopic moisture over oil of vitriol, so that the high rate at which 8 per cent. was given off cannot be explained on that hypothesis. We must see, therefore, that there is a change in the vapour-tension after one molecule of water has gone off, leaving the compound $MgSO_4.6H_2O$. The second, third, and fourth molecules come off at the same rate, but then there is another change at about 29 per cent., agreeing with a residue of the formula $MgSO_4.3H_2O$, or containing one half of the moisture of the former compound. The rate continues diminishing till we have the compound $MgSO_4.2H_2O$ left, when it becomes so slow that it is followed no further. The following table, which represents the rate of dehydration of the same salt in an air bath at 100° C., shows very plainly that the dehydration of magnesium sulphate might be pushed till only one molecule was left at 100°, if sufficient time were given. The numbers in this table are represented graphically in Curve No. III.

Temperature 100°.

Intervals.	Total time.	Loss per cent.
1 hour	1 hour	27·48
1 „	2 hours	32·01
1 „	3 „	33·22
1 „	4 „	33·70
1 „	5 „	34·42
1 „	6 „	34·95
1 „	7 „	35·17

Thus of hydrates of magnesium sulphate, we have—

Already known..........	$MgSO_4.7H_2O$
"	" $6H_2O$
New	" $3H_2O$
"	" $2H_2O$
Already known..........	" H_2O

Zinc sulphate was then examined. This salt can be partially dehydrated by standing over strong sulphuric acid at ordinary temperatures, but the dehydration proceeds very slowly. This, however, plainly shows that the zinc salt is less stable at low temperatures than the magnesium salt, and I wished especially to find whether this stability held good through a range of temperature. The salt was therefore done at the boiling point of water. The following are the results. See also Curve No. IV.

Temperature 100°.

Intervals.	Total time.	Loss per cent.
5′	0h 5′	2·32
10	0 15	3·09
60	1 15	9·70
60	2 15	19·87
30	2 45	32·52
60	3 45	34·28
120	5 45	35·73
60	6 45	35·87

Here we have the curious phenomenon of a salt losing water at an increasing rate. I was so much struck with this result, that to avoid all mistake the determination was done twice with the utmost care, and gave the same result each time. A strange feature about this salt is, that at first it does not fuse, but after three molecules of water are given off, it suddenly fuses, giving off other two molecules, and then suddenly falls to a far lower vapour-tension. In all the other cases I have as yet examined, the vapour-tension decreases as the decomposition proceeds, but in the case of zinc sulphate for the greater portion of the decomposition, the reverse is the case. In this case the salt operated upon contained 1·89 per cent. of hygroscopic moisture; so that this quantity has to be subtracted from all the numbers, in order to obtain the true amounts. Another determination gave in one hour a loss of 8·28 per cent. of moisture, which, on subtracting 1·89, leaves 6·39, a loss equal to 1 molecule, which requires 6·27. There is then no break till a loss of 3 molecules is reached, which requires 18·80 per cent. Other 2 molecules then go off, leaving $ZnSO_4.2H_2O$. The dehydration then becomes very slow till 6 molecules have gone, and there it stops. Thus we have of hydrates of zinc sulphate—

Already known	$ZnSO_4.7H_2O$
„	„ $6H_2O$
„	„ $5H_2O$
New	„ $3H_2O$
Already known	„ $2H_2O$
„	„ H_2O

It will be seen at a glance that the zinc sulphate in its mode of decomposition cannot be compared with the magnesium compound; that is to say, that although statically they are alike, dynamically they are totally different as regards their relations with water. As these sulphates form similar double salts, it is my intention to examine these salts to find if any such differences exist between them as between the simple salts, and especially to examine the salt $MgZn(SO_4)_2.14H_2O$ to find whether the two curves are merged, or whether this salt will have a dynamical mode of its own.

The other sulphate examined is ferrous sulphate, which, like the others, was examined at 100°. I found that when the air is dried by sulphuric acid, only six molecules can be driven off; but when the air is carefully desiccated over phosphoric anhydride, a portion of the seventh molecule may be expelled. I believe that this would occur with many substances at present supposed to retain moisture at 100°, and that if the tension of the vapour in the air be reduced below that of the vapour in the hydrate, the water will be given off. The following table gives the results of the examination of ferrous sulphate. See also Curve No. V.

Temperature 100°.

Intervals.	Total time.	Loss per cent.
7′	0h 7′	23·87
10	0 17	34·60
30	0 47	36·32
30	1 17	37·95
30	1 47	38·30
30	2 17	38·38
30	2 47	38·50
30	3 17	38·61
60	4 17	38·85
	Carried on with P_2O_5.	
60	5 17	38·98
60	6 17	39·17

These numbers give us two breaks in the curve, namely, at a loss of $5H_2O$, the residue giving the formula $FeSO_4.2H_2O$, and at a loss of $6H_2O$, giving $FeSO_4.H_2O$, both of which compounds were known.

The former part of the curve is much too quick to examine accurately, and would require to be re-determined at a lower temperature before any opinion could be given as to whether the other hydrates have an existence or not. The form of the curve for iron is similar to that for magnesium in its general features, the difference being that the vapour-tension of the magnesium compound is altogether lower. There is no agreement between iron and zinc.

As these allied sulphates gave results showing little agreement in their dynamical deportment, I examined two chlorides, viz., those of calcium and strontium, which, as they contain the same relative amounts of water and are similar in their deportment towards nearly all other chemical substances, seemed to offer a very good pair for examination. The calcium salt was first examined, and gave the following numbers:—

Temperature 100°.

Intervals.	Total time.	Loss per cent.
5′	0h 5′	5·27
10	0 15	8·62
10	0 25	10·01
10	0 35	11·20
10	0 45	11·89
10	0 55	12·87
10	1 5	13·45
10	1 15	14·28
15	1 30	15·30
20	1 50	16·85
30	2 20	17·71
30	2 50	20·49
30	3 20	22·22
30	3 50	23·60
40	4 30	25·82
45	5 15	27·78
60	6 15	29·63

These results are shown graphically in Curve No. VI. An examination of that curve shows us that the moisture comes off at a gradually diminishing rate, and that there is no sudden change in the rate pointing to any multiple compound, unless we accept the high rate of evolution of the first molecule as proof of the existence of a hexhydrate. No doubt if the temperature were lowered, complications might be introduced, as in sodium sulphate. An examination was then made of strontium chloride, to find whether it showed any agreement with its analogue. The following numbers are the results. See also Curve No. VII.

Temperature 100°.

Intervals.	Total time.	Loss per cent.
15′	0h 15′	12·99
15	0 30	18·75
30	1 0	27·81
30	1 30	31·25
30	2 0	32·62
60	3 0	33·90
60	4 0	34·18
60	5 0	34·28

Here again we see a regular decrease in the rate, and no points where we could expect to find a compound, unless we take the point of greatest decrease, which occurs at 27·8 per cent., which agrees very closely with a loss of $4H_2O$, leaving a residue of $SrCl_2.2H_2O$, analogous to the salt of calcium obtained by heating the hexhydrate to 100°. The salt was then dehydrated over oil of vitriol at 10°, when the following results were obtained. They are also shown graphically at Curve No. XI. It is very curious to note that the amount of moisture given off (about one half) is evolved at a constant or nearly constant rate.

Temperature 10°.

Intervals.	Total time.	Loss per cent.
1 hour	1 hour	0·357
2 hours	3 hours	0·758
1 hour	4 ,,	0·928
18 hours	22 ,,	4·68
3 ,,	25 ,,	5·39
3 ,,	28 ,,	6·02
18 ,,	46 ,,	9·23
6 ,,	52 ,,	10·84
18 ,,	70 ,,	14·24
27 ,,	97 ,,	19·31
27 ,,	124 ,,	24·36
42 ,,	166 ,,	27·57

It is thus seen that $SrCl_2.6H_2O$, dried over strong sulphuric acid, leaves a hydrate of the formula $SrCl_2.3H_2O$, and that the vapour-tension of the substance is nearly constant at 10° C. till this compound is reached. It was seen that at a higher temperature a curve representing the vapour-tension had an unbroken form, but here we see a very sudden diminution of the tension, giving a broken curve. It appears, then, from an examination of these results, that at low temperatures many more multiple-proportion compounds are formed than at high temperatures, and I think that it seems likely that were the temperature raised high enough, all sudden changes in vapour-tension would be eliminated, and an unbroken curve of hyperbolic form would represent the change in vapour-tension, or the progress of evolution of the moisture. One result which may be gained by this mode of examination of the rate of change in vapour-tension is, that we shall be able to discriminate between hygroscopic moisture and the same substance chemically combined. To refer to a case of this kind, it was supposed that air-dried silica contained a large proportion of hygroscopic moisture; but I was enabled to show, in the paper before referred to, that this moisture was evolved at a rate by many times slower at 100° than moisture undoubtedly chemically combined in other substances, so that it is erroneous to consider this moisture merely hygroscopic. It was found that if the hydrated silica be examined wet, all the "mechanical" water comes off in less than one minute; whereas the moisture which used to be considered hygroscopic is evolved at a rate at least 20 times slower, so that it can in no way be called uncombined moisture. An examination of calcium sulphate by this method gave results pointing to the existence of the compound $2CaSO4.3H_2O$. In examining this compound, experiments had to be made to determine accurately its dissociating point. It is generally stated that calcium sulphate gives off three-fourths of its water between 100° and 120°, and does not part with the last portion till between 200° and 300°. A weighed portion of pure selenite, finely powdered, was submitted to the following experiments:—It was kept for 20 minutes at each of the following temperatures, without suffering any loss—100°, 103°, 105°, 110°, 115°, 117°, but at 118° water began to come off, and after about 2 hours at 125°, it had parted with 15·28 per cent. of its moisture; but it required a temperature of 150° to complete the first stage of the decomposition, when 15·68 per cent. had been expelled, the calculated amount for $2CaSO_4.4H_2O - 3H_2O$ being 15·69. The temperature was then raised and weighings made at intervals, till it was found that the last stage of the decomposition began at 178°. The temperature was maintained at 180° for an hour, when it was found that 19·78 per cent. had been driven off. As the dissociation had ceased, the temperature was raised to 190°, when, after 30 minutes, the loss was 20·85, the calculated amount being 20·93. Thus we find that calcium sulphate may be entirely dehydrated at 190°. It was further noticed that when the first dissociation is started at 118°, if the temperature be lowered, the decomposition still goes on even at 100°, or rather at that temperature at which the vapour-tension of water equals the pressure of the atmosphere, because 15 per cent. of the water of calcium sulphate may be expelled at 99° (after starting at 118°), provided the barometer be at such a height that that is the temperature of boiling water. The following table gives the rate of dissociation of the compound:—

Time, in minutes.	Temp.	Loss.	Time, in minutes.	Temp.	Loss.
20′	118°	4·58	30′	100°	10·78
30	100	5·53			11·44
		6·20			12·11
		6·85			12·76
		7·51			13·42
		8·15			14·10
		8·82			14·76
		9·48			15·18
		10·13			15·21

These numbers are represented graphically in Curve No. XII, Plate II. We see from them that there is some indication of a compound having the formula $2CaSO_4.3H_2O$, as there is a decided change of rate after 5·53 per cent. of loss, but there is not the slightest indication of the existence of the compound $2CaSO_4.2H_2O$. It does not disprove the possibility of its existence, but as other methods have failed to form such a body, it affords further evidence of the improbability of its formation. An examination was also made of the compound $CaSO_4.Na_2SO.K_2CrO_4H_2O$.* The rate of loss is represented in the following table, and is shown graphically in Curve No. XIII, Plate II.

Temperature 100°.

Time, in minutes.	Loss.	Time, in minutes.	Loss.
15′	0·46	15′	2·46
,,	0·90	,,	2·75
,,	1·37	,,	3·07
,,	1·82	,,	3·32
,,	2·15	,,	3·58

The total water amounts to 3·63. Here we see a sudden change in the rate of dissociation, and we must, therefore, suppose that two hydrates exist, having the formulæ—

(1.) $2(CaSO_4.Na_2SO_4.K_2CrO_4).2H_2O$
(2.) $2(CaSO_4.Na_2SO_4.K_2CrO_4).H_2O$.

I hope to be able in a future communication to reduce the above numbers to vapour-tensions, and as, by this method, tensions quite imperceptible by the ordinary method can easily be measured (in fact the smaller the vapour-tension, the longer the time, and therefore the more accurate the measurement), it will be seen that the process is one which will yield results otherwise unattainable.

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* "On some Compounds of Calcium Sulphate" (p. 401 of this volume).

APPENDIX.

No.	List of Curves.	Temperature.
I	$Na_2SO_4.10H_2O$	60°
II	$MgSO_4.7H_2O$	100
III	$MgSO_4.7H_2O$	" in air.
IV	$ZnSO_4.7H_2O$	"
V	$FeSO_4.7H_2O$	"
VI	$CaCl_2.6H_2O$	"
VII	$SrCl_2.6H_2O$	"
VIII	$Na_2SO_4.10H_2O$	33°
IX	$Na_2SO_4.7H_2O$	"
X	$Na_2SO_4.10H_2O$	10°
XI	$SrCl_26H_2O$	"
XII	$CaSO_4.2H_2O$	100°
XIII	$2(CaSO_4Na_2SO_4K_2CrO_4)2H_2O$	"

The time in Plate II is to be doubled for Curve No. X, that is, time marked 6 hours is to be considered 12, and so on; and for Curve No. XI, the time is to be multiplied by 10. This is rendered necessary to prevent multiplicity of plates.

XXII.—*On the Dehydration of Hydrates by the Time Method.*

By WILLIAM RAMSAY, Ph.D.

PART I. *Iron and Aluminium Hydrates.*

THE hydrates of the metals have, as a rule, been accepted as definite substances, and have been supposed to bear analogy to the chlorides, bromides, nitrates, &c., in their formulæ; for example, it is customary to represent ferric hydrate by the formula $Fe(OH)_3$, analogous to ferric chloride, $FeCl_3$, or by the double formula, $Fe_2(OH)_6$, analogous to Fe_2Cl_6. But statements about the hydrates of iron, aluminium, chromium, and many other metals, vary so much, that it appeared desirable to revise the subject, and to ascertain under what circumstances definite hydrates, if they do indeed exist, can exist.

I am indebted to my friend, Mr. Hannay, for the principle of the method employed in this investigation; viz., to determine the loss of water of the hydrates when dried at a constant temperature, at regular intervals of time. In the case of crystalline bodies containing water, as shown by Mr. Hannay, in the preceding paper, the water is given off at a certain rate till a certain number of molecules have been expelled; the rate then changes and usually becomes slower, keeping pretty constant till a lower stage of hydration has been reached; the water is then evolved at a different rate, and this goes on till all the water of crystallisation in the salt has gone.

The following hydrates of alumina have been described:—1st. The trihydrate, $Al_2O_3.3H_2O$, obtained as a gelatinous precipitate by adding ammonia to a concentrated solution of a salt of aluminium, and drying (in air?); 2nd. The dihydrate, $Al_2O_3.2H_2O$, prepared by heating aluminium acetate to 100° for some days, and drying the resulting precipitate at 100°; 3rd. The monohydrate, $Al_2O_3.H_2O$, found native as diaspore. If these hydrates are definite chemical substances, it is to be expected that they should exhibit different vapour-tensions, and that in drying by the time method, the rate at which the water is given off should be different for each hydrate; if, on the other hand, they are not definite, the water should be expelled at a constantly decreasing rate, without showing any sudden change when the substance passes from one state of hydration to another.

The aluminium hydrate was precipitated from a boiling solution of the chloride with ammonia; the chloride had been obtained by dissolving in hydrochloric acid alumina precipitated from alum with ammonia, again precipitating as hydrate, and again dissolving. It was then washed free by decantation, not only from hydrochloric acid, but until it gave a hardly perceptible coloration with Nessler's reagent; and it was dried by exposure to air for a number of weeks. It formed a hard, horny substance, which, although it could be scratched with a knife, yet had to be reduced to powder in an agate mortar. Its composition was found to be—

$$Al_2O_3 = 54{\cdot}08 \text{ per cent.}$$
$$H_2O = 45{\cdot}92 \quad ,,$$

The formula, $Al_2O_3.5H_2O$ requires 53·33 per cent. Al_2O_3, and 46·67 per cent. of water.

The method of drying the hydrate was as follows:—A watch-glass filled with the powdered hydrate was placed in a bath, heated to a constant temperature. After a certain time had elapsed (depending on the expected loss of water), the watch-glass was removed and placed over sulphuric acid for ten minutes to cool; it was then weighed, and again placed in the bath. When the loss became so small as to be unweighable, the temperature was raised, and a new set of experiments begun.

In the accompanying graphic representation, the ordinates of the Curves I, II, III, IV, and V represent minutes; the abscissæ, the

amount of water per cent. It will be seen, by reference to the diagram, that Curve No. I splits rather above 40. This represents the fact that the hydrate, after drying for 50 minutes, contained 38·7 per cent. of water; after standing in air over night, at a temperature of 14°, it had gained 2 per cent. of water, which were given off next day at 71°, at a different rate from that at which it had been evolved originally. From this it appears probable that the water absorbed was combined less closely with the alumina than that at first given off. The rate of evolution of water at 71° differs very slightly from that at 100° (II), and it is noticeable that no break of continuity occurs. Now the hydrates, $Al_2O_3.4H_2O$ and $Al_2O_3.3H_2O$, contain respectively 41·18 per cent. and 34·43 per cent. of water; and were the vapour-tensions of these hydrates different from each other, and different from those of $Al_2O_3.5H_2O$, and of alumina at a lower degree of hydration than $3H_2O$, it is probable that a break of continuity would occur, and that the curve, instead of approximating to a straight line, would alter its direction at two distinct points. $Al_2O_3.2H_2O$ contains 25·93 per cent. of water, and $Al_2O_3.H_2O$, 14·90 per cent.; the former is passed at a temperature of 145°, without any sudden change of rate, and the latter is nearly, but not quite, reached at a temperature of 300°.

On ignition of the hydrated alumina containing 14·95 per cent. of water, the powder is moved about in a curious manner by the escaping steam; the escape of water appeared to go on of its own accord after it had been induced by application of heat, for on removing the flame, the motion of the powder did not cease. It was evidently undergoing the change from the soluble to the insoluble modification of alumina, which is possibly accompanied by evolution of heat.

Curve No. VI represents the rate at which alumina loses water over oil of vitriol. It is the result of only three measurements, each ten spaces representing one day of 24 hours. The rate, as was to be expected, is slower than at 71°, but the amount of dehydration is as great as was reached at 100°. On weighing again, after four days, it was found to have gained water, owing probably to a slight change of temperature.

The rate of loss of water of ferric hydrate is graphically represented in Curves VII, VIII, IX, X, and XI. The percentages of water required by theory for the different hydrates are these:—$Fe_2O_3.3H_2O$ requires 31·03 per cent. H_2O; $Fe_2O_3.2H_2O$, 23·46 per cent.; and $Fe_2O_3.H_2O$, 10·11 per cent. The hydrate dried in air had, on one occasion, nearly the percentage of water required by the formula $Fe_2O_3.3H_2O$; but another specimen, perfectly dry to all appearance, and so hard, that it had to be reduced to powder in an agate mortar, contained 34·00 per cent. of water. It is again evident that no sudden break of continuity occurs, except at 100°; from several experiments it resulted that the hydrate of iron, precipitated either from a cold or from a boiling solution, after being dried at 100° until no more water was evolved, had approximately the formula $Fe_2O_3.H_2O$; and this was the case, whether it was dried gradually at 50° and 75° before being heated to 100°, or whether it was placed in the water-bath in a moist condition. One of two conclusions is to be inferred from this fact; either that there exists a definite hydrate, $Fe_2O_3.H_2O$, or that the vapour-tension of water at 100° is coincidently that of the combination of ferric oxide with water at the same temperature. If a coincidence, it is a curious one.

The dotted line in Curve No. IX represents the probable course of a curve showing the loss of water by ferric hydrate at 100°. The first weighing was made after three hours' exposure to 100°.

A dotted line will also be noticed in Curve No. X. The iron hydrate, after standing over-night over oil of vitriol, absorbed nearly 1·75 per cent., which it gave off after 20 minutes' exposure to 150° much more rapidly than it had done previously. This would again point to the conclusion that the water absorbed was not in such close combination with the ferric oxide as it had previously been.

The conclusions to be drawn from these results are as follows:—If there are only four or five hydrates of iron or aluminium, their vapour-tensions do not differ much from each other (with exception of that of $Fe_2O_3.H_2O$); the probability is, however, either that hydrates, such as $Al_2O_3.4H_2O$, $Al_2O_3.3H_2O$, $Fe_2O_3.3H_2O$, &c., have no existence, or that a very large number of hydrates of aluminium and iron exist, the vapour-tensions of which are very slightly different from each other, the smallest rise or fall of temperature being sufficient to convert a higher into a lower hydrate, or *vice versâ*. It must always be understood that these conclusions apply only to the amorphous hydrates of the above-mentioned metals.

I have also made experiments on the hydrates of copper and lead with the view of ascertaining their true composition. Copper hydrate prepared by precipitating a solution of the chloride with warm baryta-water, washing the precipitate free from barium chloride, and drying in air, has the formula $CuO.H_2O$.

Water found....................	20·88 per cent.
„ calculated................	19·48 „

It loses very little water and preserves its colour at 120°, the amount of water at that temperature being 20·30 per cent. At 150° it begins to blacken and is slowly converted into the black oxide. This agrees with the results of Proust's experiments.

Lead hydrate, prepared from the nitrate by precipitation with excess of baryta-water (used because of the difficulty of washing such hydrates free from potash or soda) and washed until free from barium nitrate, contained when dried in air 4·00 per cent. of water, agreeing thus with the formula $2PbO.H_2O$, which requires 3·88 per cent. Over sulphuric acid for some weeks it lost water, but still contained 2·69 per cent., equivalent to $3PbO.H_2O$, which demands 2·71 per cent. Both of these hydrates have been prepared: $3PbO.H_2O$ by Tünnermann, from a cold solution of lead acetate and ammonia; by Payen, from a boiling solution of the same salt; and $2PbO.H_2O$ by Schaffner, from lead acetate and potassium hydrate.

I propose to extend these researches to other hydrates, the results of which I hope to have the honour of laying before the Society.

XXIII.—*On some Compounds of Calcium Sulphate.*

By J. B. Hannay, F.R.S.E.

Calcium sulphate having the character of being a difficultly soluble salt, has not—considering its important place in nature—been much investigated as to its relations to other soluble bodies, and more especially as to its relations to these bodies when passing into the crystalline state, as in the formation of double salts. For a long time the only two double salts known were those having the formulæ $CaNa_2(SO_4)_2$ and $CaNa_4(SO_4)_3 + H_2O$, the one of which was first found naturally formed, afterwards both were formed in the laboratory. It was only lately that the existence was proved of another body having the formula $CaK_2(SO_4)_2 + H_2O$, containing a potassium instead of a sodium salt; yet it has been formed in tons during the last 50 years in certain manufacturing operations, but has always been mistaken for calcium sulphate.

This body has the peculiarity that, when treated with large quantities of water, it gives up the potassium sulphate which it contains and takes up water to become normal calcium sulphate. If this calcium sulphate be again treated with potassium sulphate it again forms the double compound; in fact, it combines with whichever is in excess. I have found another compound of this double salt with water which is formed under slightly different circumstances. When a strong solution of impure potassium sulphate containing calcium sulphate is evaporated by boiling till a large quantity of granular potassium sulphate has collected, the salt referred to is formed amongst others.

It is obtained by washing away all the soluble salts with water, when a white salt, similar in appearance to steatite, is left. It gave on analysis 7·92 per cent. of water and 40·82 per cent. of $CaSO_4$, which agrees pretty well with the formula $2CaK_2(SO_4)_2 + 3H_2O$, which requires 80·1 per cent. H_2O and 40·35 per cent. $CaSO_4$. The principal difference between this salt and that before described is that water does not decompose it, except after long boiling. It is strange that, although it is formed at a higher temperature, it contains more water. The two formulæ might be stated as—

(1.) $2CaK_2(SO_4)_2 + 2H_2O$
(2.) $2CaK_2(SO_4)_2 + 3H_2O$.

Seeing from these results that calcium sulphate was capable of forming interesting compounds, I considered that in advantageous circumstances it might form many double compounds, the conditions required being that a strong solution of a salt holding $CaSO_4$ in solution be slowly cooled. I despaired of getting results in the laboratory on a small scale, owing to the difficult solubility of the salt, but I thought that in large manufacturing operations, where solutions of such a character are circulating through the same pipes for months without being disturbed, I might find some of the double salts which I considered were likely to exist. On making an examination, with this view, into layers of crystalline matter deposited upon tubes through which solutions containing simultaneously K_2SO_4, Na_2SO_4, $CaSO_4$, $MgSO_4$, and K_2CrO_4, of which the last constituted the greater portion, my search was rewarded by finding some interesting double compounds. The temperatures of the liquids varied from 40° to 80° C. Most of the layers consisted of the double salt, $CaK_2(SO_4)_2 + H_2O$, but amongst the layers I found two remarkable salts, the first of which gave on analysis 38·84 per cent. $CaSO_4$, 29·08 CrO_3, and $5{\cdot}18H_2O$, which agrees pretty well with the formula $CaSO_4 + K_2CrO_4 + H_2O$, or $K_2CaCrSO_8 + H_2O$, whilst the other gave 25·90 per cent. $CaSO_4$, and 74·12 per cent. K_2CrO_4, which is in close agreement with the formula $CaSO_4.2K_2CrO_4$, or $K_4CaCr_2SO_{12}$. These two salts were so similar to each other that they could not be distinguished as separate salts by the eye. They had a bright golden appearance, such as is possessed by iodide of lead crystallised from boiling-water. They were in flat prisms, but too confused and irregular to enable me to determine their crystalline form. When placed in pure water the crystals became white, while the solution became yellow; in fact the whole of the potassium chromate could be dissolved out without the crystal breaking up, although it became quite soft, and was really only a mass of $CaSO_4 + 2H_2O$, having the form of the crystal. Conjoined to the latter of these two salts I found a dull-coloured part, which had no definite crystalline structure, but looked like an amorphous deposit, but which the microscope showed to be composed of little interlaced needles. Two analyses of different parts of it did not give very accordant results, but the formula seemed to be $CaSO_4,Na_2SO_4K_2CrO_4$, or it may be represented as the second of the two above salts, in which one half of the potassium chromate has been replaced by sodium sulphate. In another tube, where there were large quantities of the salt $CaNa_2(SO_4)_2$ deposited, I found a salt similar to the above, but containing water. It occurred as a thick crust, with a crystalline structure radiating from the centre of the tube to the circumference. It gave on analysis as follows:—

	Found.	Calculated for $CaSO_4,Na_2,SO_4,K_2CrO_4 + H_2O$.
Ca................	8·14	8·17
K and Na..........	25·40	25·32
K.................	16·00	15·94
S.................	12·88	13·05
Cr................	10·75	10·64
H_2O..............	3·62	3·65

As will be seen, these numbers agree with the formula $CaSO_4 + Na_2SO_4 + K_2CrO_4 + H_2O$. Another set of compounds I examined was that of which the only already-known one was the acid sulphate described by Davy. I had often noticed that when a solution of calcium sulphate is boiled to dryness with hydrochloric acid, the first portions of the acid are not easily expelled, but that two or three per cent. are often retained at 120° to 130° C. On dissolving $CaSO_4$ in hydrochloric acid, and allowing it to crystallise, nothing of this kind takes place; the crystals only need pressure between bibulous paper and desiccation over oil of vitriol to entirely free them from hydrochloric acid, and leave pure crystals of the compound $CaSO_4 + 2H_2O$. Even when the solution is evaporated over the water-bath, the residue consists of needles of the pure salt. But when evaporated at a higher temperature by active ebullition at the ordinary pressure, or better under a pressure of a few pounds per square inch, the calcium sulphate retains an increasing quantity of hydrochloric acid. I conducted an experiment as follows:—The solution was placed in a bulb, and the neck drawn out to a capillary point, and the bulb heated to 116°, that is placed in a bath maintained at this temperature. The vapour escaped only under some pressure, and the evaporation was continued to dryness, when, before cooling, the residual gas was replaced by air. The substance on analysis gave the following:—On solution in nitric acid and precipitation with silver nitrate it gave 9·86 per cent. of chlorine, and another portion gave on ignition 25·10 of a total loss, while 74·90 of pure calcium sulphate remained. This is in very close agreement with the numbers required by the formula $2CaSO_4$ + $3H_2O$ + HCl, that is the normal salt $2CaSO_4$ + $4H_2O$ with one of the water molecules replaced by HCl, a most unexpected result. The numbers for the above formula are 9·79 Cl, 24·96 H_2O + HCl, and 75·04 $CaSO_4$. I intend, when opportunity offers, to extend this work, and find whether the four separate molecules may be in like manner replaced by varying the pressure and temperature. We already know, from the existence of the compound $2CaSO_4$ + H_2O, that the formula of normal calcium sulphate should be doubled, that is, it should be $2CaSO_4.4H_2O$, and it occurred to me to determine whether this could be further sustained by the isolation of the series of compounds:—

$$2CaSO_4.4H_2O$$
$$2CaSO_4.3H_2O$$
$$2CaSO_4.2H_2O$$
$$2CaSO_4.H_2O.$$

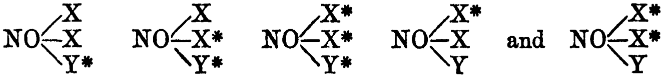
The first and last occur naturally, and are also formed by the evaporation of solutions under different conditions. I found that the evaporation of an aqueous solution of the salt at 100° gave the normal salt, whilst under a pressure of 90 lbs. per square inch, that is, at a temperature of 143°, the last alone is formed. I tried several temperatures between these, but could get no definite results. In one case alone a salt was formed which, on ignition, gave a loss of 13·22 per cent., but as this does not agree with any of the above (the third requires 11·68 per cent., and the second 15·69 per cent.), it was evidently a mixture. This method was then abandoned for the "time method," an account of which is given on page 381.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

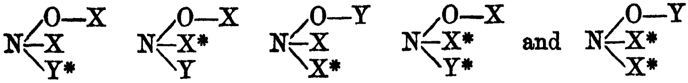
On the Theory of Chemical Affinity. By H. KOMMRATH (*Deut. Chem. Ges. Ber.*, x, 742—745).—Let it be supposed that each different kind of elementary atom possesses a force of chemical combination different from that of any other kind of atom, and that action and reaction are equal; then if a carbon-atom be united to four monad groups, X, Y, Z, &c., possessed of the respective forces, x, y, z, &c., so as to give rise to the compounds, CX_4, CY_4, CZ_4, &c., different results will follow according as the force of combination of the carbon-atom is greater than, equal to, or less than $4x$, $4y$, $4z$, &c. Thus, if C be the force of the carbon atom, and $C > 4x$, only one modification of the compound is possible; if, however, $C < 4x$, various modifications are possible, inasmuch as there must be one at least of the four monad groups united by a weaker force than the others, this weaker force being equal to $C - 3x$ in the case where $C > 3x$, and when only one of the four atoms is thus united by a weaker force. According as one or more of the monad atoms are thus united by a force less than that normally due to them, different isomeric modifications must result.

To apply this to the hydroxylamine derivatives of Lossen, if these bodies are indicated by the formula, $N\begin{matrix}=O\\-X\\-X\\-Y\end{matrix}$, and if the force of combination of the group NO is either greater than or equal to the forces of the radicles $2X + Y$ jointly, only one compound is possible; but if $NO < 2X + Y$, there may be several isomeric modifications, viz.:—



where the radicles marked * are united by less powerful forces; and among these again there may be innumerable modifications of the second and third, according to the relative diminutions in the forces x and y.

If the formula $\left(N\begin{matrix}-O-\\-\\-\end{matrix}\right)\begin{matrix}X\\X\\Y\end{matrix}$ be employed, there are only two isomerides when N—O— is greater than or equal to $2X + Y$, viz., $N\begin{matrix}-O-Y\\-X\\-X\end{matrix}$, and $N\begin{matrix}-O-X\\-X\\-Y\end{matrix}$; but if $(N-O-) < 2X + Y$, five cases again occur, viz.:—



The identity between amyl-ethylaniline and ethyl-amylaniline found by Hofmann shows only that $C_5H_{11} + C_2H_5 + C_6H_5 \leqq N$; if, however, this relationship, $a + b + c \leqq d$, did not hold, isomeric modifications might exist. No conclusion can therefore be drawn from Hofmann's results as to the equality in atom-fixing powers of the different "bonds" of nitrogen. C. R. A. W.

The Law of Avogadro and Ampère. By A. WURTZ (*Compt. rend.*, lxxxiv, 977—983).—The experiments on the constitution of the vapour of chloral hydrate at 78°, which were made by Troost with Hofmann's apparatus, have been repeated by the author. The latter conducted his experiments under as nearly as possible the same conditions as Troost; but by avoiding the introduction of hygroscopic moisture with the potassium oxalate, he obtained results which lead to the exactly opposite conclusion, namely, that in the vapour of chloral hydrate, the water and the chloral are dissociated. He instituted comparative experiments between the vapour of hydrate of chloral on the one hand, and a mixture of air and aqueous vapour on the other, in which the tension of the latter was exactly equal to that of the aqueous vapour in the dissociated hydrate of chloral. Similar apparatus contained the two mixtures, which were exposed to the same temperature and pressure, such, namely, that the tension of the aqueous vapour might be equal to, or slightly higher than, the tension of dissociation of neutral potassium oxalate. The introduction of this salt increased the tension by only a few millimeters in each case, proving that the hydrate of chloral vapour contained aqueous vapour. The author strongly contends for the validity of the law of Avogadro and Ampère, against the attacks which have been made upon it by Deville and others. R. R.

A Modification of Vapour-Density Determination. By G. GOLDSCHMIEDT and G. CIAMICIAN (*Deut. Chem. Ges. Ber.*, x, 641—646).—The authors have modified v. Meyer's method (this Journal, 1877, i, 34) to make it applicable for temperatures below 100°, and give drawings of their apparatus. C. S.

Volume-Constitution of Solids. By H. SCHRÖDER (*Deut. Chem. Ges. Ber.*, x, 848—853).—The following values were found:—

	V.
Silver acetate	51·3—51·8
Silver butyrate	82·9
Silver isovalerate	99·0
Silver oxalate	60·3
Silver succinate	86·2—87·2

The difference of volume in the fatty acids is, therefore, 15·8 for each CH_2; a similar difference is shown, according to Topsöe's investigation, by the double chlorides of gold and diethylamine ($v = 169·1$) and trimethylamine ($v = 200·3$). If C and H have the same volume, we have $C = H = 5·2$.

The volume of silver carbonate is 46, differing from that of the oxalate by 15·0, and the difference between silver oxide and carbonate is 15·2; or $CO = CO_2 = CH_2 = 3 \times 5·1$.

	V.
Succinic acid	75·3
Hydrated oxalic acid	76·4
Tartaric acid	85·5

The two former are therefore isosteric, or $C = O$, and the difference between succinic and tartaric shows $O = 5·2$. Silver oxalate is also isosteric with silver selenate and chromate.

In silver oxide ($v = 30·8$) Ag is probably $= 10·28$; if, therefore, in the following formulæ, the number of atoms is given by the lower, and that of the units of volume $= 5·14$ by the upper number, we find $Ag^4_2O^2_1 = 30·8$. In the fatty acids, one atom of oxygen appears to occupy two volumes:—

$$C^2_2Ag^2_1H^3_3O^3_2 = 51·3$$
$$C^4_4Ag^2_1H^7_7O^3_2 = 82·9$$
$$C^5_5Ag^2_1H^9_9O^3_2 = 98·7$$

The relations between the volume-constitutions of the oxalates and tartrates of the alkali-metals of the carbonates and formates of lead and barium, and chloride, iodide, and telluride of silver, are also pointed out. C. S.

Molecular Changes. By J. v. JONSTORFF (*Deut. Chem. Ges. Ber.*, x, 866—867).—Crystals of iodine, having a diameter of 2—3 mm., which were kept in a dark place for eight years, at a temperature from 0°—24°, were found to have increased to a diameter from 4—5 mm. Pure amorphous phosphorus, kept under water for nine years, was partly changed into minute crystals of white phosphorus. C. S.

Diathermaneity of Metals and Paper. By M. AYMOUNET (*Compt. rend.*, lxxxiv, 259—260).—The experiments of MM. Wiedmann and Frantz relating to the coefficient of conductivity of metals, and on the rapidity with which an equilibrium of temperature is established in metallic bars, combined with similar experiments made by the author, in which paper was employed, show—

1. That metals and paper are not athermanous, as is generally believed.
2. That they are more diathermanous for dark rays emanating from

metallic substances at a temperature lower than 100°, than for rays which are luminous, or at a temperature approaching redness.

3. That their absorbing powers are less than that of water.

4. That it is possible to find a mathematical relation between the absorbing power of a body and its coefficient of conductivity.

J. W.

Inorganic Chemistry.

Action of Alkaline Copper Solution on Hydroxylamine. By JULIUS DONATH (*Deut. Chem. Ges. Ber.*, x, 766—772).—When hydroxylamine hydrochloride is decomposed by Fehling's solution in excess, the reaction is indicated by the equation—

$$2NH_3O + O_2 = 3H_2O + N_2O,$$

the amount of nitrous oxide is almost the theoretical quantity; traces of ammonia, however, are formed. The author regards the formula $H_3N{<}\genfrac{}{}{0pt}{}{O}{O}{>}NH_3$ as applicable to hydroxylamine.

C. R. A. W.

Trihydroxyl-antimonic Acid, Pyroantimonic Acid, and Oxychloride of Antimony. By H. DAUBRAWA (*Liebig's Annalen*, clxxxvi, 110—122).—The analogy between the compounds of phosphorus and antimony, together with the results obtained by Geuther, Frémy, and other chemists, renders the existence of bodies corresponding with H_3PO_4 and $POCl_3$ at least highly probable. The author added antimony pentachloride, drop by drop, to water, kept at a temperature of 16·5°, and obtained a white precipitate which was filtered off and washed with water at 17°, till the filtrate no longer contained hydrochloric acid. This was pressed between filter-paper and dried on a plate of gypsum till it became perfectly white and opaque. A part of it was next further dried over sulphuric acid, and then ignited in a glass-tube. The results of analysis showed that the air-dried body consisted of $H_8Sb_2O_9$ (Frémy, $H_4Sb_2O_7 + 2H_2O$); when dried over sulphuric acid it consisted of $H_6Sb_2O_8$ (Frémy, $H_4Sb_2O_7 + H_2O$); dried at 100°, of $H_4Sb_2O_7$: when heated to 200° it was converted into metantimonic acid, $HSbO_3$; at 275° it passed into pentoxide, Sb_2O_5, and above 300° into tetroxide of antimony, Sb_2O_4. Possibly this is the acid of the antimony series which corresponds with H_3PO_4. The following experiment shows the existence of a body $SbOCl_3$ analogous to $POCl_3$. Sixteen parts by weight of antimony pentachloride were added drop by drop to one part of water kept cool by ice. A yellowish crystalline mass was thus obtained, which could be kept unaltered in dry air. This body melts when heated to a clear yellowish liquid, and finally boils, giving off dense vapours, and becoming white and crystalline when cold. Possibly dissociation takes place on heating—$SbOCl_3$ becoming $SbOCl$ and Cl_2, which latter escapes. No water is deposited in the colder part of the tube—a proof that the elements of water are entirely absorbed in the reaction, and that the body formed does not consist of $SbCl_5 + 4H_2O$. The following equations indicate the way in which the $SbOCl_3$ may be formed and undergo decomposition:—

$$SbCl_5 + H_2O = SbOCl_3 + 2HCl,$$

$$SbOCl_3 + Na_2CO_3 = SbOCl + Cl_2 + Na_2CO_3 = SbOCl + 2NaCl + O + CO_2,$$

$$2SbOCl + Na_2CO_3 = 2NaCl + CO_2 + Sb_2O_3.$$

Antimony oxytrichloride added to alcohol dissolves at once to a clear liquid, which, when evaporated on the water-bath, evolves hydrochloric acid, and finally yields a mass of yellow crystals grouped in rosettes. If water is added to this residue, a smell of alcohol is developed, and a white precipitate is thrown down. Perhaps a triethylantimoniate is formed, with separation of hydrochloric acid, and on addition of water alcohol is regenerated and antimonic acid set free. G. T. A.

Salts of Chromium Sesquioxide. By A. ETARD (*Compt. rend.*, lxxxiv, 1089—92).—The author, without throwing doubt on the existence of the chromium sulphate prepared by Schroeder, and, according to him having the formula $Cr_2(SO_4)_3.15H_2O$, has been led, by the analogy and isomorphism of the salts of chromium and aluminum, to prepare a sulphate of chromium containing 18 molecules of water. This salt he prepares by acting on a solution of 100 pts. of CrO_3 in 150 pts. H_2SO_4 and 225 pts. of water with vapour of ether; the crystals which form are collected, dried on porous plates, and washed with ether. The sulphate obtained is a violet salt of definite composition, crystallising in plates, and remaining unchanged in the air. At ordinary temperatures it contains $Cr_2(SO_4)_2 18H_2O$, losing 30·5 of its weight at 100°, becoming converted, by loss of $12H_2O$, into a green crystalline sulphate, $Cr_2(SO_4)_3 6H_2O$, which is deliquescent and convertible into the anhydrous salt at a dull red heat. Thus the composition of the violet sulphate would be expressed by the formula $Cr_2(SO_4)_3 = 6H_2O.12Aq$.

By comparing these formulæ the author thinks that the violet colour is due to superhydration of the salts. Frémy having shown, with regard to the hydrated chromium oxides, that the violet may be changed to the green modifications by other means than heat, *e.g.*, desiccation in a vacuum or gentle friction, the author tried to obtain similar transformations of the sulphate. Under these circumstances violet sulphate in a fine state of division becomes green in contact with dehydrating liquids, as fuming HNO_3, H_2SO_4 and PCl_3. Only those salts can be called green which appear so by artificial transmitted light, as those which may appear quite green by direct sunlight show the presence of a large proportion of the violet salt when viewed by transmitted light. The violet phosphate containing $12H_2O$ is transformed into green phosphate with $5H_2O$ at 100°, and behaves similarly to the violet sulphate with fuming nitric and sulphuric acids.

The author has also prepared a crystalline salt, $Cr_2(SO_4)_6K_6$, or $Cr_2O_3.3SO_3 + 3(K_2O.SO_3)$, which is very stable and represents one molecule of anhydrous Cr_2Cl_6 in which the chlorine is replaced by six proportions of K_2SO_4. He proposes to name this salt *potassio-sulphate of chromium*, and prepares it by the gradual addition of anhydrous Cr_2Cl_6 to molten potassium bisulphate, the excess of this latter being extracted with water, leaving the double salt in the form of furry needles of a greenish-yellow colour. A nitro-sulphate of chromium has also been obtained, as well as analogous salts of iron. It is to be remarked that the relation between the acid in the sesquisulphate and that in the alkaline salt is the same as that in the triple magnesian sulphates. J. M. T.

Sulphide of Manganese. By DE CLERMONT and GUIOT (*Bull. Soc. Chim.* [2], xxvii, 353—359).—The change of colour from flesh tint to sulphur-yellow observed in sulphide of manganese has already been the subject of much investigation. The authors have made several experiments, which have led them not only to discover several new cases of the occurrence of this change, but several also where it has been stated not to take place, in which, nevertheless, they observed it. When the compound was heated under pressure, even as high as 305° for 48 hours, in presence of much water, the colour underwent no alteration; but when only a little water was present, the sulphur-yellow colour soon appeared. This shows that water-vapour soon effects the change, but that water itself, at however high a temperature, does not. The transformation is not effected by heating the rose-coloured sulphide to considerable temperatures either dry, by itself, or with solutions of caustic potash or potassium chloride. In the two latter cases white manganese compounds are ultimately produced. The same negative effect is produced by the action of sodium-amalgam and soda. On heating the manganese sulphide with strong ammonia in the air, or with ammonium chloride and quicklime under pressure, no change is effected, whereas the yellow colour appears when the sulphide is heated with ammonia-solution under pressure. This would seem to indicate that ammonia gas does not act under pressure, except when water is present.

When manganese sulphide is dissolved in ammonia oxalate, a yellow liquid is obtained containing ammonium sulphide and manganese oxalate. Precipitated by an excess of ammonium sulphide, this yields rose-coloured sulphide of manganese, which turns green on boiling for some time. If ammonia be added previously, the precipitation no longer takes place in the cold, but on heating, the rose-coloured sulphide is precipitated, passing rapidly to green.

In presence of ammonia the rose-coloured sulphide is precipitated from the same yellow liquid, passing rapidly to dark green. The different results obtained by How and Muck (*Chem. News*, xix, 137) may be attributed solely to the presence of ammonium chloride in their reactions.

In heating the rose-coloured sulphide with ammonium oxalate under pressure no change takes place if the oxalate is in excess; but if the sulphide is in excess, it turns to green. Under the like conditions, ammonium sulphate produces no change; ammonium carbonate and phosphate form the corresponding manganese salts.

Protracted boiling with hydrosulphuric acid in the air produces no change, but under pressure, at a temperature of 220°, the green colour appears.

None of the alkaline sulphides produce any change under any conditions. Potassium persulphide turns the manganese sulphide violet; a mixture of equal parts of potassium or sodium sulphide and ammonium sulphide, in excess, and under pressure, rapidly changes the rose to green.

Muck asserts that manganese carbonate cannot be converted into the green sulphide. The authors heated some carefully prepared manganese carbonate with an excess of ammonium sulphide in the air, and in 10 minutes obtained a fine green sulphide. The change was completed by heating under pressure. Alkaline sulphides had no effect; neither had sulphuric acid under any condition. If a stream of carbonic anhydride or well-dried ammonia be passed into a tube containing a little boat full of the rose-coloured sulphide, the transformation is effected in a short time with the aid of a Bunsen burner. The colour is grey-green when hot, becoming of a fine green when cooled in a current of the gas.

Geuther affirms that freezing changes the rose colour to green. The authors confirm the contrary assertion of Muck, having tried numerous experiments at low temperatures with different mixtures, either of the rose sulphide with other bodies, as ammonium sulphide and carbonate and ammonia solution, or such bodies as would by their combination produce the rose-coloured sulphide. In no case was the change effected. The authors contradict the assertion of Muck that the green sulphide is an oxysulphide, the change having been effected by them out of contact with any oxidizing agent, and when it was effected in a measured volume of air no diminution whatever was discernible. Neither can they confirm the assertion of Muck that the green sulphide contains 7 per cent. of water, an experiment made by them with great care having shown the loss to be under 0·5 per cent.

The rose-coloured sulphide is a hydrated body, as a portion of it, treated in precisely the same way as the green, suffered loss equivalent to 9 per cent. The solubility of the two sulphides in ammonia salts differs also considerably, a series of careful experiments having shown the rose-coloured sulphide to be five times as soluble in ammonium chloride as the green. From the fact of the rose-coloured sulphide being amorphous while the green is crystalline, the authors imagined that phosphorescence might attend the change, but no luminosity could be observed. Both sulphides when dry, or covered with water, resist oxidation, but if they are compressed and moistened, the temperature is considerably raised and water vapour evolved.

The authors made several attempts to convert the green sulphide into the rose-coloured, but without success. They came to the conclusion that the two bodies are the same sulphide in different degrees of hydration. C. L. F.

Mineralogical Chemistry.

Strengite, a New Mineral. By A. Nies (*Jahrb. f. Min.*, 1877, 8—16).—This mineral occurs in an isolated ironstone and psilomelane-block in the silicious slate of the great brown iron-ore deposit of Dünsberg, near Giessen, in globular, reniform, and radio-fibrous aggregations, having a drusy surface and often accompanied by very fine cacoxene. On rare occasions isolated crystals are found, possessing a strong vitreous lustre. These crystals are transparent or translucent, red in various shades (pomegranate-red and carmine-red), also white, and occasionally colourless; streak, yellowish-white; H. 3—4; spec. grav. 2·87. Before the blowpipe the mineral fuses easily to a black, shining globule, colours the flame bluish-green, and gives the reactions for iron; on heating it in the matrass much water is evolved, whilst hydrochloric acid dissolves it easily, especially when hot, but it is not easily attacked by nitric acid. In order to obtain pure material for analysis, selected portions of the mineral were treated with stannous chloride solution, which dissolved out the brown iron-ore and left the small isolated crystals of strengite behind. An analysis of these showed the mineral to have the following composition:—

Fe_2O_3.	P_2O_5.	H_2O.
43·18	37·42	19·40 = 100·00

from which the formula $Fe_2O_3P_2O_5 + 4H_2O$ is obtained. Strengite belongs therefore to the same class of minerals as scorodite ($Fe_2O_3As_2O_5 + 4H_2O$) and the barrandite of von Zeparovich $\left\{\begin{matrix}\frac{4}{7}Fe_2O_3\\ \frac{3}{7}Al_2O_3\end{matrix}\right\} P_2O_5 + 4H_2O$; it crystallises in the rhombic system, but it was extremely difficult to determine the forms with accuracy, owing to the imperfect lustre on the faces. The forms observed in combination were $\infty P\infty . \infty\breve{P}2.P.m\breve{P}\infty$; the latter could not be accurately determined. Cleavage indistinct, parallel to $\infty\bar{P}\infty$, a pearly, vitreous lustre characterising the cleavage planes. The habit of isolated crystals is "thin-tabular" through $\infty\bar{P}\infty$, but the commonest occurrence is a sheaf-like aggregation on which only the faces of P are visible. Numerous measurements of the crystals were made, with the following results:—

Angle of the terminal edge of P in the macrodiagonal = 102° 14′
" " " brachydiagonal = 115° 8′
Angle of the prism .... = 118° 36′

Mean ratio of the lengths of the axes obtained from the above measurements, $a : b : c = 1 : 1·1855 : 1·1224$, whence are calculated the angles as follows, viz.:—

Macrodiagonal terminal edge of P = 101° 38′
Brachydiagonal " " = 115° 36′
Lateral edge of P .... = 111° 30′

These calculated angles agree very closely with the measurements obtained with scorodite by Briethaupt, Miller, von Zeparovich, von Kokscharow, and vom Rath, viz.:—

Macrodiagonal terminal edge of P = 102° 28′
Brachydiagonal „ „ = 114° 28′
Lateral edge of P............. = 111° 42′

It appears therefore that strengite and scorodite are isomorphous. Their resemblance in form and occurrence is very striking, and the author points to their complete isomorphism as a further proof of the close analogy of arsenic acid and phosphoric acid to each other. He also considers it probable that they are the final members of the series of phosphatic minerals to which pyromorphite and mimetesite belong. The author named the mineral "strengite," in honour of Prof. Streng, of Giessen. C. A. B.

The Microscopical Discrimination of Nephelin and Apatite. By A. Streng (*Jahrb. f. Min.*, 1877, 94—95).—As both the above minerals exhibit identical physical characteristics under the microscope, they can be distinguished from each other only by chemical means. A thin section of the mineral supposed to contain apatite is treated (whilst under the microscope) with a drop of ammonium molybdate solution in nitric acid, when the characteristic yellow precipitate immediately appears encircling isolated apatite crystals. In the immediate neighbourhood of the crystals, or upon them, no precipitate is observed, which agrees with the well-known fact that the yellow precipitate never forms in presence of excess of phosphoric acid. Respecting the appearance of this well-known precipitate under the microscope little need be said, the precipitate consisting of regular octohedrons and rhombic dodecahedrons, which, on increased growth, sometimes become covered with globular or reniform masses of the same substance. *Nephelin* may be detected in the most certain and beautiful manner simply by treating a thin section of the mineral supposed to contain it under the microscope with strong hydrochloric acid, when the nephelin crystals will dissolve, and after some time has elapsed, cubical crystals of sodium chloride will be observed in the hollows where the nephelin crystals were formerly situated. The sodium chloride is formed by the decomposition of the sodium silicate, and separates out owing to its insolubility in hydrochloric acid. C. A. B.

Remarks on Fischer's Communications upon Cat's-eye Quartz. By F. Hornstein (*Jahrb. f. Min.* 1877, 96—97).—The author agrees with Fischer in concluding that the fibrous structure of the so-called "cat's-eye quartz" is due to pseudomorphous quartz formation after asbestos, and not, as was formerly supposed, to the interpolation of asbestos fibres. At the same time Hornstein ascertained from his own investigations upon specimens from Hof and Treseburg that the peculiar shimmering appearance observed on this mineral was due to the actual presence of interpolated asbestos fibres, therefore in his opinion Fischer was in error when he stated that asbestos was not present in any specimens. C. A. B.

Ærinite and Ginilsite. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1877, 97—98).—Ærinite is a massive dark-blue mineral, which appears to be homogeneous and covered with a film of hydrated ferric oxide, sp. gr. 2·670. Before the blowpipe it loses colour and fuses on the edges to a dark or light glass. The two analyses made showed it to have the following composition:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Loss on ignition.	
(1)	42·92	15·34	7·12	3·16	15·40	2·45	12·07 =	98·46
(2)	44·00	15·39	8·88	3·16	13·88	2·44	13·00 =	100·75

Ginilsite from the Ginil Alp, in Graubündten, is a greyish-yellow mineral, sp. gr. 3·404. Chemical composition—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	
37·83	7·77	15·63	26·67	9·73	3·30 =	100·93

C. A. B.

Structure and Mineralogical Composition of Variolite from Durance. By A. MICHEL LEVY (*Compt. rend.*, lxxxiv, 264—266).—The author has studied the nature of the globular structure and petrographic affinities of this rock. With respect to quartziferous porphyries, the occurrence of spherolites appears without doubt to be intimately associated with the excess of silica contained in these rocks; such, however, does not seem to be the case with variolite, which not only does not contain excess of silica, but is, moreover, according to many authorities, associated, at least in position, with euphotide; this, however, is denied by some mineralogists, who differ also a good deal in opinion respecting the composition and structure of its globular constituents.

By the aid of the microscope, and by attacking thin plates with hydrofluoric acid, the author has shown that the globules are perfectly crystalline, and that elementary felspathic fibres, apparently related to oligoclase, may be detected in them; the felspathic element is shown by its refractive index and percentage of silica and alkali; while the identity with oligoclase is proved by the fact that this mineral is the only felspar which, like the specimen under examination, has an axis of optical elasticity approximatively coinciding with one of the axes of figure.

The fibres of oligoclase are generally separated from each other by rows of granules of pyroxene, and by layers of actinote, while the basis of the variolite consists of the same pyroxenic globules, lamellar actinote, and hornblende; besides these three latter constituents there is generally a small quantity of an ill-defined green amorphous substance. Vacuoles or cavities invariably exist in variolite, which have been subsequently filled up with labradorite, needles of actinote, or pyroxene.

The form of the globules is not strictly circular, but more or less arborescent, which distinguishes them from petrosiliceous globules properly so called; as before mentioned, they are surrounded by granules of pyroxene, which define with great clearness the most delicate ramifications.

Beginning with the oldest constituents, the order of consolidation of the various elements of variolite is as follows:—pyroxene granules and lamellar actinote of the globules; elementary fibres of oligoclase; actinote and hornblende of the base. The globules become distinct before the end of the semi-solid condition, while the vacuoles, due to disengagement of gas, were produced before the felspathic matter of the globules; lastly, the basis of the rock was consolidated in successive zones around the globules and vacuoles. The crystallisation of the actinote of the base is supposed to be of still later date.

The author's conclusions are opposed to those of Zirkel: he considers that the evidence is sufficient to show that the globules of variolite are not petrosiliceous, and that the rock forms a complete term of the series known as euphotides. J. W.

Chemical Constitution of Leadhillite. By LASPEYRES (*J. pr. Chem.* [2], xv, 317—319).—The former analyses of Irving, Berzelius, Stromeyer, and Thomson were made on leadhillite from Scotland, that of Kotschubey on a mineral from Nertschinsk, and that of Bertram on a specimen from Sardinia: all agree with the formula $Pb_4SC_3O_{13}$, or $3PbCO_3 + PbSO_4$. Hintze has, however, shown that the Scotch mineral contains water; the author confirms this, and finds, moreover, that the crystalline form is monoclinic, not rhombic, and that in composition and crystallographic character it is identical with *maxite*, the formula—

$$H_{10}Pb_{18}C_9S_5O_{56}, \text{ or } 5PbSO_4, 9PbCO_3, 4PbO, 5H_2O$$

indicating both substances. C. R. A. W.

Chemical Examination of the "Contact-zones" of the Aluminous Slate and Granite-block of Barr-Andlau. By H. UNGER (*Jahrb. f. Min.*, 1876, 785—807). Professor Rosenbusch described the metamorphic aluminous slate of the Barr-Andlau district (*Jahrb. f. Min.*, 1875, 849), and the author was entrusted with the chemical portion of the examination, which is embodied in the present communication. Carius (*Ann. Chem. Pharm.*, xciv, 45) described a metamorphosed aluminous slate from Eichgrün, Saxony, and could not distinguish any difference in the chemical composition either of the original or the metamorphosed rock, excepting, perhaps, a diminution in the amount of combined water in the latter. Carius did not deduce anything from his examination. Fikenscher (*Metamorphische Gesteine der Lunzenauer Schieferhalbinsel*, Leipzig, 1867) also found great constancy in the chemical composition of the rocks, but he concluded from his results that the active agents in the changes observed were *an increased temperature and steam*. C. W. C. Fuchs (*Die alten Sedimentformationen und ihre Metamorphose in den franz. Pyrenäen*. Jahrb. f. Min., 1870, 719—752, and 851—879) concludes from his investigations:—1. That the metamorphosis occurs without any difference in chemical composition up to a certain degree; (2) that the metamorphosis of the mica-slate and gneiss of the Pyrenees is mainly due to chemical action, there being occasionally an addition or a loss of a constituent, viz., in the aluminous slates and true mica-slates a loss in the amount of alkaline earths and iron, and an increase in the alkalis and silica. The author wished to ascertain what chemical relationship existed between the metamorphic aluminous slate and the granite penetrating it, submitting all the specimens to petrographical examination and accurate chemical analysis, beginning with the unaltered aluminous slate, then passing on through different stages of alteration until the metamorphosis was complete.

(1.) *Steiger-slate* (*Steiger-schiefer*).—A very soft normal aluminous slate; slatey structure distinct, reddish-brown colour, silky lustre on the slatey surfaces; occasionally indistinctly foliated and penetrated by veins of quartz. Sp. gr. 2·790. It contained 1·54 per cent. of hygroscopical water, and had the following composition:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
57·320	traces	25·270	6·430	1·308	0·220	1·050	0·660

K_2O.	Na_2O.	H_2O.
2·582	2·170	3·770 = 100·780

From this analysis is obtained the relation existing between R_2O, RO, R_2O_3, and SiO_2, viz., $(R_2O + RO) : R_2O_3 : SiO_2$.
$1·140 : 1 : 3·314$,
pointing to this slate being a mixture of mica, quartz, and a silicate containing less alumina than mica.

(2.) *Slate from the Littelsbacher-thal, near Hohwald* (*Steiger-schiefer*) corresponds almost exactly with the one already mentioned. Sp. gr. 2·812.

(3.) *Nodular slate from between Dudenbach and Hasselbach-thal* (*Knoten-schiefer*).—Slatey structure distinct, greyish-brown colour, slightly softer than ordinary aluminous slate, and penetrated by small black spots. Hygroscopic water 0·519 per cent. Sp. gr. 2·828. Its composition was as follows:—

SiO.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.
63·87	22·12	7·28	1·08	traces	0·09	0·06	1·63	0·97

H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
3·51 = 100·61	0·935	1	4·076

(4.) *Nodular slate from the Andlau-thal.*—Slatey structure only very indistinct, light-grey colour, and penetrated by numerous black spots, Hygroscopical water 1·038 per cent. Sp. gr. 2·831. Chemical composition as follows:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
60·20	traces	27·09	3·38	2·22	traces	0·95	0·65	1·245

Na_2O.	H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
0·470	4·40 = 100·65	0·689	1	2·104

(5.) *Nodular slate from between Dudelbach and the Hasselbach-thal,* closely resembles the last described slate in colour and habit, excepting that the characteristic nodules (Knoten) are very prominent. Hygroscopical water 0·57 per cent. Sp. gr. 2·789. Chemical composition as follows:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
58·28	trace	20·77	7·79	1·94	trace	2·57	1·86	3·44

Na_2O.	H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
1·24	3·39 = 101·28	1·441	1	3·849

(6.) *Passage of the "Nodular slate" to Andalusitic slate, from the Andlauthal.*—The slatey structure discernible only on weathered spots. The rock is densely penetrated by black spots, but owing to the dark colour of the ground-mass they do not appear very prominent. Particles of mica can be detected with a lens. Colour, reddish-brown. Hygroscopical water 0·52 per cent. Sp. gr. 2·850. Chemical composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
56·680	27·900	6·377	0·290	trace	0·710	1·070	3·765

Na_2O.	H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
0·826	2·700 = 100·318	0·787	1	3·015

(7.) *Andalusitic slate from the Kiehnberg.*—Hygroscopical water 0·24 per cent. Sp. gr. 2·820. Chemical composition as follows:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	FeO.	CaO.	MgO.
58·810	trace	24·383	7·380	0·201	0·495	0·890	1·700

K_2O.	Na_2O.	H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
2·509	0·983	2·170 = 100·615	0·387	1	3·437

(8.) *Andalusitic slate from Landsberg.*—Hygroscopical water 0·107. Sp. gr. 2·773. Chemical composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
54·11	30·77	3·500	6·010	trace	1·510	1·180	0·878

Na_2O.	H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
1·210	1·450 = 100·618	0·827	1	2·788

(9.) *Andalusitic slate from between Landsberg and Kiehnberg.*—Hygroscopical water 0·07 per cent. Sp. gr. 2·823. Chemical composition:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
58·273	0·190	25·378	5·382	5·148	trace	0·820	2·596	trace

Na_2O.	H_2O.	$R_2O + RO$.	R_2O_3.	SiO_2.
trace	1·990 = 99·777	0·926	1	3·448

In order to ascertain the quantitative mineralogical composition of these rocks, the last-mentioned specimen was digested for 24 hours with hydrochloric acid of sp. gr. 1·09, evaporated to dryness, redissolved in hydrochloric acid and water, filtered, and analysed; the soluble portion consisting of the following percentages:—

TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.
0·197	9·380	5·382	5·148	0·357	2·244

The insoluble residue was well boiled with caustic soda solution, and the silica thus dissolved was estimated to be 11·870 per cent. The residue from the latter solution was then fused with sodium carbonate, and analysed, furnishing the following percentages:—

SiO_2.	Al_2O_3.	CaO.	MgO.
45·990	15·998	0·352	0·174

36·756 per cent. of the silica was insoluble, and, therefore, calculated as quartz. From the results thus obtained, the author calculated the percentage amounts of the various minerals entering into the composition of the specimen in question to be as follows, viz.:—

Titanic iron	0·7380 per cent.
Magnetic iron............	7·2616 ,,
Magnesia mica (Biotite) ..	27·5590 ,,
Andalusite	24·7881 ,,
Quartz	36·7560 ,,
	97·1027

This agrees sufficiently well with the analysis.

Granite.—This rock penetrates the above-mentioned slates, and is the cause of the metamorphism observed in them. It is a normal porphyritic granitite. The quartz is slightly red in colour, full of fluid enclosures and long, colourless, acicular apatite.

The predominating felspar is red and monosymmetrical; but with the naked eye it is evident that there is an interpolation of colourless lamellæ of unysmmetrical felspar. The mica is black and rich in iron (Biotite), but occasionally partially altered into a green chloritic substance. The accessory minerals are magnetite and titanic iron. An analysis of the granitite showed it to have the following composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	TiO_2.	CaO.	MgO.
68·967	14·797	2·320	0·850	0·010	0·309	3·815	1·150

K_2O.	Na_2O.	H_2O.
4·538	2·460	0·707 = 99·923

Sp. gr. 2·6800. Owing to the lamellar development observed on the felspar it was thought advisable to submit it to analysis. The following was the result:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
66·852	18·432	1·082	0·084	0·022	11·475	2·958	0·033 = 100·938

From this analysis the author considers the mineralogical constitution of this specimen to be as follows:—

Kaolin	0·2355	per cent.
Magnesia mica	0·3066	,,
Hematite	1·0380	,,
Orthoclase	67·9360	,,
Albite	24·6720	,,
Anorthite	0·3060	,,
Quartz	5·6520	,,
	100·1461	

The mineralogical constitution of the granitite (omitting the small quantity of water) appears approximately to be as follows, viz.:—

Orthoclase	35·1372	per cent.
Albite	31·2982	,,
Titanic iron	1·0441	,,
Quartz	24·5430	,,
Magnesia mica	10·6946	,,
Hematite	1·6480	,,
	104·3651	

The difference in the amounts of Al_2O_3 obtained by calculation and experiment may be accounted for by "weathering," which was observed to have taken place.

Deductions from the foregoing Work.—(1.) The unaltered and metamorphosed slates consist of the same original chemical substances, and were not altered by the loss or addition of any constituent, but more probably by a molecular transformation.

(2.) The andalusitic slate has the following mineralogical constitution, viz.:—

Titanic iron	0·7	per cent.
Magnetic iron	7·2	,,
Magnesia mica	32·4	,,
Andalusite	24·7	,,
Quartz	36·3	,,
	101·3	

(3.) The granitite which penetrated the aluminous slates is a normal one.

(4.) The orthoclase of the granitite contains sodium felspar (albite), and calcium-sodium felspar (anorthite-albite).

(5.) The contact-phenomena on the steiger-slate most closely resemble those of the slates from Voigtland described by Naumann, approaching also in many particulars the slates of Lunzenau and the Pyrenees.

(6.) All endeavours to bring about an artificial alteration of the slates in question were unsuccessful, but some crystalline bodies were obtained, which, however, did not correspond with any of the minerals observed in the slates or the granitite. C. A. B.

Presence of Mercury in the Spring "du Rocher" at the Establishment of Mont Carnadore (Saint Nectaire-le-Haut, Puy-de-Dôme). By Garrigou (*Compt. rend.*, lxxxiv, 963—965.)—The analysis was made with about 500 litres of water, with the following result per litre:—

Carbonic acid	1·8878
Sulphuric „	0·2658
Silicic „	0·2458
Phosphoric „	distinct traces.
Boracic „	
Nitric „	
Chlorine	1·0992
Iodine	0·0002
Soda	2·9999
Potash	0·1069
Lithia	0·0213
Ammonia	0·0005
Lime	0·2068
Strontia	distinct traces.
Baryta	
Magnesia	0·1225
Alumina	0·0096
Chromic oxide and glucina	trace.
Iron (sesquioxide)	0·1180
Manganese do.	0·0057
Zinc	0·0005
Cobalt, nickel, copper, lead, silver, mercury, arsenic, antimony, tin about	0·0080
Organic matter about	0·0580

This water proved beneficial to a person affected with syphilis, possibly on account of the mercury. Enough mercury was obtained to exhibit in the metallic state.

W. R.

Organic Chemistry.

The Doctrine of Limits in the Formation of Ethers, a Contribution to our Knowledge of Etherification. By J. H. van't Hoff (*Deut. Chem. Ges. Ber.*, x, 669—678).—As a considerable amount of work has lately been done on the question of the speed of chemical reactions, the author of this paper thinks that it may not be out of place to raise a question which bears close relation to it, and the explanation of which may be best treated from a mathematical point of view. It bears a close relation to the extensive work of Berthelot and Péan de St. Giles, by which it has been made clear under various circumstances, what quantity of acid in contact with a fixed quantity of alcohol becomes converted into ether.

The converse may be solved at the same time, viz., the quantity of an alcohol capable of the formation of ether under the action of a fixed quantity of acid.

The mathematical consideration of this problem is somewhat interesting, as by observation it is found that a simple solution is possible for all cases, and may be stated in the following manner:

Within certain limits the maximum of ether formed is independent of the temperature.

The different acids behave approximately in the same manner; for instance, if the same number of molecules of two different acids are added to the same quantity of alcohol, the same amount of each is capable of forming ether. The different alcohols behave in the same way.

Alcohol and acid behave nearly similarly, viz., a certain quantity of acid molecules being brought in contact with a double quantity of alcohol, the circumstances being the same in both cases, then taking acid instead of alcohol, or *vice versâ*, similar quantities of ether will be formed.

A quantity of ether added at the commencement influences the new formation of this substance in almost the same manner as a corresponding greater addition of water.

The maximum quantity of ether formed is independent of neutral bodies added to the mixture. It is also independent of the whole volume occupied by the mixture.

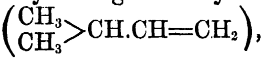
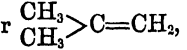
For the experimental tables and the mathematical equations, reference must be made to the original paper.

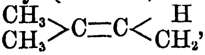
From these the conclusion may be drawn that the mathematical reasoning gives a true representation of the reactions under nearly all possible circumstances. The author lays particular value on his first-mentioned averages (page 675), as in this case the large number of the experiments shows the differences in the results, and that the numbers found by calculation lie exactly between those experimentally determined. Although hydrates of the alcohols and acids must necessarily have been formed, they could not be taken into consideration, as the whole of this subject is still doubtful. If the reactions of these last were only known qualitatively, it could then be discussed in the limit equation.

J. M. T.

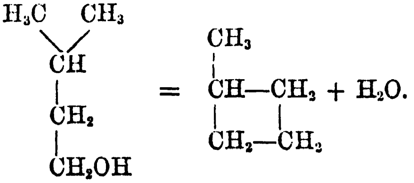
A Process of Solidification of Carbon-disulphide. By M. MERCIER (*Compt. rend.*, lxxxiv, 916—917).—Drying oils, such as boiled linseed oil, on treatment with a small quantity (10 p.c.) of sulphur chloride, solidify to a transparent elastic substance containing sulphur. If carbon disulphide be added at the moment of solidification, a gelatinous mass is formed containing 10 p.c. of disulphide. The jelly does not melt at 100°, and is difficult to ignite. The carbon disulphide is gradually evolved on standing. The vapour-tension of this compound is 218 mm. at 19°, and the mercury falls slowly; with carbon disulphide the mercury falls at once to 282 mm.

W. R.

Structure of the Isomeric Amylenes. By A. WISCHNEGRADSKY and F. FLAWITZKY (*Deut. Chem. Ges. Ber.*, x, 404—407).—Owing to the contradictory results obtained by various other chemists, Wischnegradsky determined to prepare, synthetically, dimethyl-ethyl carbinol and methyl-isopropyl carbinol, and to compare their derivatives with those of the different amylenes. The dimethyl-ethyl carbinol prepared from chloropropionyl and zinc-methyl, boils constantly at 102·5°, and solidifies at —12°. The boiling-point of its chloride is 86°, of the bromide, between 108° and 109°, and of the iodide, 128—129°. By the action of oxidising agents, it is converted into acetone and acetic acid. The secondary alcohol was obtained by reduction of the corresponding ketone by means of sodium-amalgam. The boiling-point of this alcohol was found to be 112·5°, and not 108° as Münch gives it. It does not solidify in a freezing mixture of snow and calcium chloride. By oxidation it furnishes methyl-isopropyl ketone, acetic acid, and acetone. Gaseous hydriodic and hydrochloric acids, and also phosphorus pentachloride, convert the alcohol at ordinary temperatures into the corresponding derivatives of the tertiary amyl-alcohol. This behaviour inclines Wischnegradsky to the belief that a simple substitution of hydroxyl by halogen does not take place, but rather a hydro-halogen addition takes place on the part of the hydrocarbon, which is formed by elimination of water. This supposition is supported by the fact that even on treating the alcohol with dilute hydriodic acid (the reaction takes place at 100°), amylene and diamylene are formed. Methyl-isopropyl-carbinol is, therefore, not in the position to yield secondary halogen-derivatives. These can, however, be obtained in another way. If gaseous hydriodic acid be passed into Flawitzky's amylene  $\left(\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH.CH{=}CH_2\right)$, about 40 per cent. only of the hydrocarbon becomes combined with the acid, whilst a pentylene boiling constantly at 21·1—21·3° remains behind. This pentylene is identical with the amylene from ethyl-amyl-oxide. The iodide formed is identical with the tertiary iodide. The hydrocarbon unattacked combines slowly with hydriodic acid to form an iodide boiling at 137—139°. With hydrobromic acid, Flawitzky's amylene behaves similarly. In this case two bromides are obtained, one boiling at 108° and the other at 115—116°. The hydrocarbon combines only at a high temperature with hydrochloric acid, and thus it was found impossible to obtain the secondary chloride. The pentylene boiling at 21°, when subjected to the special treatment, does not form methyl-isopropyl carbinol, but is converted into the tertiary amyl alcohol. There is now no doubt that the amylene hydrate which Flawitzky prepared is a tertiary alcohol, that he obtained only tertiary derivatives from his amylene, and that his pentylene is a mixture of two isomeric hydrocarbons (boiling point = 23—27°). One of them (boiling at 21·1—21·3°) is isopropylethylene $(CH_3)_2.CH.CH{=}CH_2$, as only this hydrocarbon can yield the derivatives of methyl-isopropyl carbinol. As to the other pentylene, it might be either $(CH_3)_2.C = CH.CH_3$, or  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{=}CH_2$, either of these hydrocarbons directly yielding the tertiary amyl-compounds. The obtaining of the first of these isomerides could be explained on the assumption that the isopropylethene, directly obtained by the action of alcoholic potash on the iodide of fermentation amyl alcohol is partially converted into the isomeric trimethyl-ethene. If, however, this supposition were true, then the optically inactive amyl iodide (from amyl-ethyl oxide) must also furnish two hydrocarbons. This is not so, and hence the second formula for the pentylene in question must be chosen, and the ground for its formation be sought for, in the chemical duality of fermentation amyl alcohol. Ossipoff states that by treating commercial amylene with sulphuric acid of different strengths, he obtained, by the action of the stronger acid, an alcohol boiling at 99°, which he considers to be dimethyl-ethyl carbinol, and with weaker acid, an alcohol boiling at 102—105°, to which he assigns the formula $(CH_3)_2CH.CH.OH.CH_3$. Wischnegradsky, on repeating these experiments, has obtained in both cases tertiary amyl alcohol. W. S.

Behaviour of various Amylenes to Oxidising Agents. By Fr. Zeidler (*Liebig's Annalen*, clxxxvi, 245—256).—The various amylenes were subjected to the action of potassium permanganate, chromic acid, potassium chromate, potassium iodate, and nitric acid, the same conditions being maintained in each case. The operation was performed in sealed tubes, heat being applied, when no rise of temperature took place of itself. The first amylene examined was prepared from optically inactive amyl alcohol by the action of fused zinc chloride. The acids obtained by the various oxidising agents, were succinic, oxalic, butyric, propionic, acetic, formic and carbonic. The second amylene (boiling-point 22—23°) was prepared by heating amyl iodide (obtained from optically inactive amyl alcohol), with an alcoholic solution of caustic soda. The oxidation-products consisted of succinic, oxalic, butyric, propionic, acetic, and carbonic acids. A third amylene (boiling at about 33°), prepared by the action of phosphorus pentoxide on ethyl-amyl ether, yielded, on oxidation, oxalic, propionic, acetic, formic, and carbonic acids. In no case could either valeric or pyrotartaric acid be detected. The products of oxidation of the first amylene stand in contradiction to the formula assigned to it by Flavitzky (*Annalen*, clxxix, 340), since from a body of the constitution  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C{=}C\!<\!\begin{matrix}H\\CH_2\end{matrix}$, it would be difficult to explain the formation of succinic and butyric acids.

The author thinks that this formula belongs to the third of the above amylenes, which is not identical with the first one. By the action of zinc chloride on amyl alcohol, a closed ring is probably formed, as is shown in the following equation:—



G. T. A.

Thallene. By H. MORTON (*Pogg. Ann.*, clx, 655—656).—The author draws attention to the fact that he first isolated and described this substance in 1872. It is obtained from the last products which come over in the distillation of the American petroleums. Its composition is identical with that of anthracene, but its physical and chemical properties show that it is an entirely different substance. Some products shown under various names at the recent Exhibition at Philadelphia, were found by the author to consist of more or less impure thallene. R. R.

Action of Water on the Haloïd Compounds of the Alcohol Radicles (Mono- and Di-haloïd Paraffins). By GUSTAV NIEDERIST (*Liebig's Annalen*, clxxxvii, 388).—When iodoethane and 15 parts of water are heated in sealed tubes to 100° for 15 hours, almost the theoretical quantities of alcohol and hydriodic acid are formed; analogous results are obtained with more or less ease with bromethane, isoiodopropane, isoiodobutane, isochlorobutane, and chloropentane (from fermentation alcohol); iodopentane almost resists the action of water at 130°. Dibromethane (ethene dibromide) can in this way be made to yield almost the theoretical amount of glycol, no resin being produced. The process is specially convenient for the preparation of pseudopropylic alcohol. C. R. A. W.

Carbon Chlorobromide from Trichloracetic Acid. By J. H. VAN'T HOFF (*Deut. Chem. Ges. Ber.*, x, 678).—In some researches on the decomposition of the carboxyl group of the halogens, the author found that potassium trichloracetate underwent decomposition with bromine in a simple manner, according to the equation—

$$CCl_3.CO_2K + Br_2 = CCl_3Br + CO_2 + KBr.$$

The decomposition was accomplished in seven hours, by heating to 110—120° in sealed tubes. The product obtained exceeded 70 per cent. of the theoretical mixture, and gave a nearly pure product. On analysis, 0·2408 gram gave 0·086 gram CO_2 = 6·164 p. c. carbon, theory requiring 6·04. The potassium salt is not easily decomposed by chlorine or iodine chloride; even after continuing the action for some time, only a heavy oil was produced, evidently CCl_4. By means of iodine a body crystallising from ether was obtained, the properties of which showed it to be C_2Cl_6. These results seem to point to the fact that the carbon chloriodide, CCl_3I at first formed is decomposed like carbon chlorobromide. J. M. T.

Action of Silver Oxalate on Ethene and Propene Bromides. By KARETNIKOFF (*Deut. Chem. Ges. Ber.*, x, 410).—By the action of silver oxalate on methene iodide, benzylidene dichloride, ethene iodide, or amylene bromide, no oxalic ethers are formed. It is now also found that ethene and propene bromides form no exception to this already known rule. The only products are, besides silver, bromine and carbon dioxide; in the one case ethene, and in the other propene.

W. S.

New Formation of Iodoform, Bromoform, &c. By C. RICE (*Chem. Centr.*, 1876, 468).—If alcohol be added to a mixture of iodine and white precipitate, violent explosion takes place, due to formation of nitrogen iodide; if, however, an alcoholic solution of iodine be added to white precipitate, explosion takes place, but with less violence. If phenol (5 grams) be added to an alcoholic solution of iodine containing 8 grams of iodine, and this mixture added to 12 grams of white precipitate, pure nitrogen is evolved, and a white sediment and iodoform remain; the sediment is dimercurammonium chloride. The aromatic liquid, on addition of water, yields a copious precipitate, from which ether extracts iodoform and mercuric iodide, separable by means of potassium iodide. The rest of the yellow precipitate appears to be a mixture of HgI and Hg_2I_3. The yield of iodoform is about 2 p. c. of the iodine used. Bromoform and chloroform may be prepared in like manner. E. W. P.

Compounds of Mercuric Cyanide with the Chlorides of the Earth Metals. By J. E. AHLEN (*Bull. Soc. Chim.*, xxvii, 365).—The following bodies, represented by the formula, $M_2Cl_6.6Hg(CN)_2 + 16H_2O$ (where M = Ce, La, Di, Y, and Er), are obtained by crystallisation from a solution of mercury cyanide with an excess of the respective chlorides. They are all very soluble, and lose their water of crystallisation at 100°, and over oil of vitriol. They crystallise only from solutions containing an excess of the chloride.

Cerium salt: tough, asbestos-like needles.

Lanthanum salt: colourless, silky needles.

Didymium salt: rose-coloured, elastic needles.

Yttrium salt: colourless, radiate and well defined prisms, losing 3 mols. H_2O over oil of vitriol.

Erbium salt: reddish, resembling the preceding.

The author has endeavoured, but unsuccessfully, to obtain double salts of mercuric cyanide and the nitrates of the earth-metals.

C. L. F.

Pure Commercial Potassium Cyanide. By C. MOLDENHAUER (*Zeitschr. Anal. Chem.*, xvi, 199).—The method proposed in the *American Chemist* (v, 396), of digesting in carbon disulphide, whereby the cyanide only is dissolved, is found in Muspratt-Stohmann's *Chemistry*. According to the author, however, potassium cyanide is insoluble in carbon disulphide. M. M. P. M.

On the Cyanides of Acid Radicles. I. By L. CLAISEN (*Deut. Chem. Ges. Ber.*, x, 429—431).—The author has obtained, by the action of fuming hydrochloric acid on benzoyl cyanide, an acid agreeing in composition with the formula, $C_8H_6O_3$. This acid melts at 65—66°, and when more strongly heated boils, with partial decomposition, into carbon dioxide and benzaldehyde. It is extremely easily soluble in water. The investigation is being continued. J. R.

Action of Nascent Thiocyanic Acid on Alcohol. By ERNST BLANKENHORN (*Deut. Chem. Ges. Ber.*, x, 445—448).—When phosphorus trichloride (or, better, a saturated solution of hydrogen chloride in alcohol) is added to a hot concentrated alcoholic solution of potassium thiocyanate, potassium chloride is deposited, and a new body, having the empirical formula $C_4H_8N_2S_2O$, is formed. The reaction probably takes place as follows:—

$$HCl + KCNS = KCl + HCNS;$$
$$2HCNS + C_2H_5OH = C_4H_8N_2S_2O.$$

The product crystallises in small, white, silky needles, which dissolve in alcohol and ether, and sparingly in water. It melts between 170° and 175°. When heated to 100° with alcoholic ammonia in sealed tubes, it yields thiocarbamide. It is being more fully investigated.

J. R.

Monochloromethyl Oxide. By C. FRIEDEL (*Compt. rend.*, lxxxiv, 247—250).—Seeing that in many organic compounds, especially in those possessing a particular chemical function, it is customary to recognise a certain definite grouping of atoms, which is peculiar to, or characteristic of the function, as for instance in the primary alcohols, aldehydes, and acids, in which the groupings $CH_2.OH$, CHO, and $CO.OH$ respectively are recognised, it was not unreasonable to suppose that, if a new or similar grouping could be obtained, it would possess distinctive properties, and that a new chemical function would correspond with it, the study of which would be of special interest. With the hope of preparing such a grouping, the action of chlorine upon methyl oxide was examined.

The monochloro-derivative of this substance should contain the grouping $(CH_2ClO)'$, in which an atom of carbon would be united directly to hydrogen, chlorine, and oxygen. The properties of such a group would probably be intermediate between those of the primary alcohol chlorides, characterised by the group CH_2Cl, and those of the acid chlorides, characterised by the group $COCl$; while the substitution of HO would most likely produce a compound possessing well marked acid qualities.

No difficulty was experienced in preparing the monochloro-derivative by the direct action of chlorine on methyl oxide. It is a limpid liquid, boiling at 59·7°, under 759 mm. pressure, with an odour resembling that of acetyl chloride. It is heavier than water, and dissolves therein, with elevation of temperature and partial decomposition, producing hydrochloric acid, methyl alcohol, and oxymethylene. It breaks up in a similar manner when treated with alkalis, so that, notwithstanding that every precaution was taken to moderate the energy of the decomposition, it was found impossible to replace the Cl by HO. The reaction with dry potassium acetate, however, was more manageable, and a liquid was obtained, boiling between 117° and 118°, in which the chlorine was replaced by oxacetyl; the compound so produced was a sort of methylal, having the formula, $CH_2\left\{\begin{matrix}OCH_3\\OC_2H_3O\end{matrix}\right.$. It is slowly decomposed by water and by alkalis, with formation of oxmethylene; with ammonia it produces, as does also the chloro-derivative, a salt of hexmethylenamine.

J. W.

Freezing Point of Ether. By A. P. N. FRANCHIMONT (*Deut. Chem. Ges. Ber.*, x, 830—831).—Fourcroy and Vauquelin have stated that ether begins to solidify at −31°, and forms at −44° a solid, crystalline mass. This statement is found in many modern books, although Thénard and Mitschell showed that pure ether does not solidify at these temperatures, nor even at −99° according to the latter. The author has found that this is correct; pure anhydrous ether contained in tubes closed with drying tubes, remained quite mobile in a mixture of solid carbon dioxide and ether. But if the tubes were only closed with corks, moisture entered, and white flakes separated at −45°. In ether containing water a larger quantity of these white crystalline flakes is formed, but it was impossible to solidify completely ether which was saturated with water, showing that it does not form a hydrate. C. S.

Essential Oil of the Fruit of Heracleum Sphondylium. By W. MÖSLINGER (*Liebig's Annalen*, clxxxv, 26—49).—126 kilos. of seeds collected in autumn, 1874, gave 1,163 grams of oil, and 173·16 kilos. from autumn 1875 yielded 1460·5 grams.

This oil consists, as Zincke has shown, chiefly of octyl acetate with a smaller quantity of caproate and a little free octyl alcohol. The latter body could not be detected by the author, who found, in addition to the two others, also octyl caproate and laurate, a small quantity of ethyl butyrate and of a hexyl ether consisting most probably of the acetate. C. S.

Behaviour of certain Ketones to Oxidising Agents. By M. HERCZ (*Liebig's Annalen*, clxxxvi, 257).—The object of this investigation was to determine in what manner ketones are acted upon by different oxidising agents; whether with different methods of oxidation and the same ketone, different oxidation-products are obtainable, or whether the so-called law of Popoff be universally true or not.

Potassium bichromate, free chromic acid (hitherto used for oxidising the ketones), potassium permanganate in neutral, acid, and alkaline solutions, silver oxide in presence of bromine, and peroxide of lead and nitric acid were all experimented with as oxidising agents. The ketones used were dimethyl ketone, methyl-propyl ketone, butyrone, caprone, and palmitone. Only so much of the oxidising agent was used, that two atoms of oxygen came in contact with one molecule of the ketone. Weighed quantities of the ketone with the proportional quantity of oxidising agent and measured quantities of water, were enclosed in sealed tubes and heated. In each glass tube almost one gram of ketone was placed. On opening the tubes, the possible presence of carbon dioxide was looked to, the volatile acids formed were set free by distilling the contents with sulphuric acid; these were then converted into silver-salts, and their nature determined by analysis of the successive fractions obtained on crystallising out the silver-salts.

I. *Oxidation of Dimethyl Ketone.*—The above-named oxidising agents were used, and acetic and carbonic acids were obtained as constant oxidation-products. In the experiments with potassium permanganate and with silver oxide and bromine, formic acid was also recognised in small quantities. Dumas and Stas have already found that acetic acid and carbonic acid are formed when acetone is oxidised by means of potassium bichromate and sulphuric acid; Gottlieb also has noted the formation of acetic acid by oxidation with free chromic acid. The results of Péan de St. Gilles are by no means confirmed, when he states that acetone is not altered on boiling with solid potassium permanganate—in fact, just the contrary was found to be the case.

II. *Oxidation of Methyl-propyl Ketone.*—The oxidation of this ketone with potassium bichromate and sulphuric acid has been already investigated by Wurtz and Schorlemmer. The former finds propionic and acetic acids as the oxidation-products, the latter obtains the same products, together with carbonic acid. The author's results confirm those of Schorlemmer.

III. *Oxidation of Butyrone.*—In agreement with the results obtained by Wurtz, butyric and propionic acids were obtained as the chief products of oxidation with potassium bichromate and sulphuric acid. In all the other oxidations also, butyric and propionic acids were uniformly obtained. Acetic acid and carbonic acids were also detected. Friedel's assertion is called in question, that only butyric acid is obtained by oxidation of butyrone with potassium permanganate in a neutral solution.

IV. *Oxidation of Caprone.*—Caproic and valeric acids appear to be the chief products; butyric, propionic, acetic and carbonic acids the secondary products of the oxidation of caprone. It is noteworthy that lower fatty acids are formed, some of the ketone remaining unaltered. Thus the Popoff law does not in this case appear quite to hold good. An oxidation with bromine and silver oxide led to no results. The action of bromine alone gave rise to a derivative of caprone. This is a brominated oxidation-product, namely, $C_{11}H_{16}Br_2O_3$, and is stated to be formed as follows:—

$$C_{11}H_{22}O + Br_{12} + 2H_2O = C_{11}H_{16}Br_2O_3 + 10HBr.$$

V. *Oxidation of Palmitone.*—The difficulty found in oxidising the higher ketones rendered it necessary (as in the case also of caprone), to use an excess of the oxidising agent. When potassium bichromate and sulphuric acid were employed, the oxidation mixture was completely reduced only after 120 hours' heating at 100—110°. On opening the tubes, carbon dioxide escaped. The contents consisted of unaltered palmitone and the chromium salts of the higher fatty acids formed. Myristic acid appeared to predominate amongst these acids. Lauric and capric acids also appear to have been formed.

When potassium permanganate was used in acid solution, a very small quantity of ketone was oxidised, and the quantity of solid fat-acids obtained was far too small to admit of a separation. In the aqueous portion of the tube-contents acetic and carbonic acids were found.

With nitric acid and lead peroxide, acetic, butyric, and propionic acids, and also carbonic acid were formed. Amongst the solid acids, one free from, and the other containing nitrogen, were found, but these could not be separated. A new brominated product was obtained as follows:—The ketone was melted on the water-bath and bromine added drop by drop. A yellow oil was thus obtained, hydrobromic acid being evolved. This was washed with ammoniacal water, and afterwards with alcohol, in which it is almost insoluble. On dissolving in ether, and evaporating, a yellow oil separated, which solidified in a freezing mixture, and possessed a melting point of 5·5°. Analyses agreed with either of the following formulæ: $C_{31}H_{59}Br_3O$ or $C_{31}H_{61}Br_3O$, presenting respectively tribromopalmitone or dibromopalmitone hydrobromide. The latter is considered the correct formula, as in another experiment dibromopalmitone itself was obtained melting at 55°.

The author confirms the following facts:—(1.) The Popoff rule, as follows: "In the oxidation of the ketones, normal acids being formed, the radical poorer in carbon remains combined with the CO= group, and by the attachment of an OH group, forms a fatty acid, whilst the radical of the ketone richer in carbon gives rise to the second fatty acid. (2.) In the formation of these primary oxidation-products the process never remains stationary, no matter what oxidising agent is employed, and in what atomic proportion the oxygen is presented." In all cases a further oxidation of the primary products takes place, and the acids to be expected according to Popoff's rule, are probably formed together with lower fatty acids and carbonic acid. In opposition to the statement of Chapman and W. Thorpe, and also of Popoff, that "the fatty acids are not acted on, or only very slightly, by potassium bichromate and sulphuric acid," it is positively affirmed that a fatty acid brought in contact with excess of sulphuric acid and some potassium bichromate solution, immediately begins to suffer oxidation. (3.) The oxidation of the ketones rich in carbon is more difficult and less complete, the higher the ketone is in the series. Palmitone, for example, yielded results so unexpected as to make it appear almost credible that palmitic acid is not a normal acid. W. S.

Monochloracetones. By A. Étard (*Compt. rend.*, lxxxiv, 951—953).—Chromyl chloride, CrO_2Cl_2, acts on amyl chloride or hydride to form monochlorobutylacetone boiling above 120°. The two substances are mixed and kept cold, and the ketone separates as an oil on addition of water. It has a peculiar aromatic smell, and attacks the eyes; boils at 120° with partial decomposition. It is insoluble in water and potash, is oxidised by chromic acid, and reduces ammoniacal silver nitrate, but does not combine with alkaline bisulphites. Inactive amyl chloride being represented by the formula $CH_2Cl—CH_2—CH(CH_3)_2$, that of monochlorobutyl-acetone becomes $CH_2Cl—CO—CH(CH_3)_2$ [isopropyl-chloromethyl-ketone].

The reaction is general, hexyl and heptyl chlorides and hydrides having been converted in a similar manner into ketones. W. R.

Pinacone and Pincacolin from Methylethyl Ketone. By G. Lawrinowitsch (*Liebig's Annalen*, clxxxv, 123—128).—Acetone when acted on by nascent hydrogen yields pinacone, which in turn, under the influence of weak acids, loses water and is converted into pinacolin. For this and other reasons pinacolin must be regarded as a ketone containing on the one hand CH_3, on the other tertiary butyl, and during its formation from acetone a methyl-group must change from one carbon-atom to another. The author undertook the preparation of a pinacone and pinacolin from methyl-ethyl ketone, in order to determine whether it is the methyl or the ethyl which suffers this change.

To prepare the pinacone, methyl-ethyl ketone was placed in a series of flasks containing a concentrated solution of potash, and pieces of sodium were introduced into each. When the reaction was over, the liquid separated from the alkaline solution was submitted to fractional distillation. Pinacone passed over between 200° and 205°. This was converted into pinacolin by means of weak sulphuric acid (one part of acid to one of water). On oxidation with bichromate of potash and sulphuric acid, the pinacolin yielded acetic acid, and an oily acid body forming a silver salt of the composition $C_6H_{11}AgO_2$.

Since the constitution of pinacolin may be expressed as—

$$\begin{array}{l} C(CH_3)_2C_2H_5 \\ CO \\ C_2H_5 \end{array} \quad \text{or as} \quad \begin{array}{l} C(C_2H_5)_2CH_3 \\ CO \\ CH_3 \end{array}$$

it ought to yield on oxidation, in the first case dimethylethylacetic acid and acetic acid, in the second diethylmethylacetic acid and carbonic acid. The body prepared by the author must therefore have the constitution expressed by the first of the above formulæ. In this case it is identical with the pinacolin of Wischnegradsky, prepared from zinc ethide and dimethylethylacetic acid. G. T. A.

Nitrosotriacetonamine. By W. HEINTZ (*Liebig's Annalen*, clxxxv, 1—13).—On mixing neutral aqueous solutions of triacetonamine hydrochloride and potassium nitrite, and heating for one or two hours to 75—80°, a reddish-brown oil separates out, which solidifies on cooling, and some of the same compound separates from the aqueous liquid, in long, slender needles. This body is *nitrosotriacetonamine*, $C_7H_{16}H_2O_2$; it melts at 72—73°, dissolves readily in alcohol, ether, and hot water, and can be sublimed. On heating it with aqueous potash, it is converted into a yellowish oil, which is also formed by boiling the nitroso-compound with water, and appears to be phorone. On heating nitrosotriacetonamine with hydrochloric acid other bases are formed, but no triacetonamine. C. S.

Acid Acetates. By H. LESCŒUR (*Compt. rend.*, lxxxiv, 1029—1031).—The paper describes the preparation of various acetates of sodium from supersaturated solutions containing acetic acid of various strengths. The author concludes from the results of his experiments that the only acid salts formed by sodium acetate and acetic acid are Berthelot's triacetate, $NaO.C_2H_3O.2C_2H_4O_2$, the cubic biacetate, $NaO.C_2H_3O_2.C_2H_4O_2$, and perhaps a sesqui-acetate. The other acid salts which have been described either have no distinct existence, or are compounds of a different order. R. R.

A New Series of Acid Salts. By A. VILLIERS (*Compt. rend.*, lxxxiv, 774—776).—By leaving hot solutions of sodium acetate containing water and acetic acid in different proportions to cool, crystals are obtained in which acetic acid plays a part analogous to that of the water of crystallisation, which in many instances it replaces in equivalent quantities. These crystals, when exposed to the air, rapidly effloresce by losing acetic acid and water. Fragments of the crystals thrown on the surface of water exhibit movements of rotation and translation, which are the more rapid as the quantity of contained acetic acid is greater. The author has obtained sodium biacetate in cubic crystals, corresponding with the potassium salt already known, and he has also prepared divers new acetates of other metals.

R. R.

On so-called Non-saturated Compounds. By R. FITTIG (*Deut. Chem. Ges. Ber.*, x, 513—522).—*The Acids in Roman Chamomile Oil.*—The acids obtained by saponification of Roman chamomile oil may be separated by fractional distillation into a liquid which boils at 160°, and two crystalline acids, angelic and tiglic. The liquid consists essentially of isobutyric acid, but contains also a small quantity of methacrylic acid.

Other acids, and especially valerianic acid, could not be detected in the specimen under examination. Demarçay has shown (*Compt. rend.*, 83, 906), that angelic acid may be converted into the isomeric tiglic acid by the aid of heat or by concentrated sulphuric acid, and concludes that only angelic acid is contained in Roman chamomile oil, the tiglic acid being formed during the distillation. The author adduces several reasons to show that this is not the case, and especially he has separated the several constituents of the part of the oil which boils below 210° by fractional distillation into four parts. The first of these, boiling at 147—148°, and the least in quantity, contains a compound ether and a hydrocarbon; on saponification it yields only isobutyric acid. The second part, boiling at 177—178°, has the formula $C_9H_{16}O_2$, and on saponification forms only angelic acid and a butyl alcohol, which boils at 105—110°. The third part boiling at 200—201°, and the fourth at 204—205°, could not be perfectly separated. Both gave on analysis numbers which indicate the formula $C_{10}H_{18}O_2$, and both yielded on saponification a mixture of angelic and tiglic acids which could easily be separated by conversion into their calcium salts, since calcic angelate is much more easily soluble than calcium tiglate. By this means the part boiling at 200—201° was found to yield little tiglic and much angelic acid, while that which boils at 204—205° yielded much tiglic and little angelic acid. The alcohol obtained from both parts boils at 130—135°, but has not yet been examined.

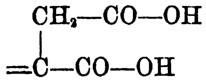
With respect to the addition-products of the two acids, it was found that when the theoretical quantity of bromine dissolved in carbon disulphide was added to the acids dissolved in the same liquid, tiglic acid yielded a solid dibromide, while angelic acid yielded only 65 per cent. of the theoretical quantity of the solid compound, but left behind a liquid part the nature of which has not yet been determined. The solid dibromide has in each case the same properties and melting point. Both acids combine directly with hydrobromic acid to form addition-products, which possess the same properties and melt at 66—66·5°. Should future experiments show that these bromine-compounds are identical, an isomeric relation will be indicated, which from the point of view giving rise to these investigations (see this Journal, 1876, i, 897) will require minute study.

The relation of Fumaric to Maleic, and of Citraconic to Mesaconic Acid.—It has been shown that maleic and fumaric acids form with fuming hydrobromic acid the same bromosuccinic acid, but that the union takes place, in the case of maleic acid at ordinary temperatures, in that of fumaric acid at 100°. Citraconic acid and mesaconic acid behave in a similar manner. Both yield the same bromopyrotartaric acid, but citraconic acid does so at ordinary temperatures, mesaconic acid only on heating in a tube. They behave similarly on their union with hydrochloric acid; with bromine also citraconic acid forms a compound at ordinary temperatures, mesaconic acid only on heating. Citradibromopyrotartaric acid melts at 150° and is decomposed at 165—170°; mesadibromopyrotartaric acid melts at 170° and undergoes decomposition. The citra-acid is also twice as easily soluble as the mesa-acid. Both acids also split up on boiling with water into bromomethacrylic acid, carbonic acid, and hydrobromic acid, but the mesa-acid does so more slowly than the citra-acid.

The analogy in behaviour of maleic and fumaric acids and of citraconic and mesaconic acids is perfect. The similarly constituted acids give with bromine different, with hydrogen and hydracids the same addition-products. These facts cannot be explained on the hypothesis that in the unsaturated compounds the carbon-atoms are always united by manifold bonds, but they lead to the supposition that compounds can exist in which, as in carbonic oxide, the combining capacities of the several carbon-atoms are not fully satisfied.

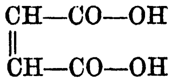
The hypothesis of polymerism does not explain them, and in the case of fumaric and maleic acids is contradicted by their vapour-densities. Nor is the supposition that on heating with hydracids mesaconic acid is converted into citraconic acid tenable, for one need only evaporate a solution of citraconic acid mixed with concentrated hydrochloric or hydrobromic acid to convert it perfectly into mesaconic acid.

But if we suppose these isomeric acids to have the constitution expressed by the formulæ—



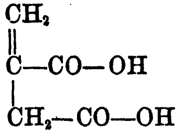
$$\begin{array}{l} \mathrm{CH_2{-}CO{-}OH} \\ | \\ \mathrm{{=}C{-}CO{-}OH} \end{array}$$

Maleic acid.



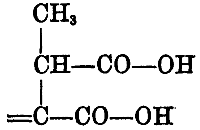
$$\begin{array}{l} \mathrm{CH{-}CO{-}OH} \\ \| \\ \mathrm{CH{-}CO{-}OH} \end{array}$$

Fumaric acid.



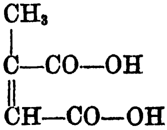
$$\begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{C{-}CO{-}OH} \\ | \\ \mathrm{CH_2{-}CO{-}OH} \end{array}$$

Itaconic acid.



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH{-}CO{-}OH} \\ | \\ \mathrm{{=}C{-}CO{-}OH} \end{array}$$

Citraconic acid.



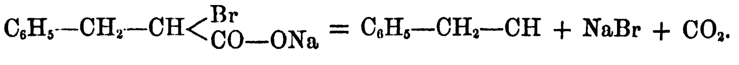
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{C{-}CO{-}OH} \\ \| \\ \mathrm{CH{-}CO{-}OH} \end{array}$$

Mesaconic acid.

all the facts hitherto observed are explained at once. By addition of bromine different products, by addition of hydrogen identical products must be formed; and by union with hydrobromic or hydrochloric acid, the same bodies can be produced. It is easy thus to understand why citra- and mesadibromopyrotartaric acids yield the same products when boiled with water, and why mesaconic acid forms addition-products with so much less facility than citraconic acid. In apparent contradiction to this view is the existence of two bromomaleic acids, but isobromomaleic acid is undoubtedly bromofumaric acid; dibromomaleic acid is dibromofumaric acid, and dioxymaleic acid is dioxyfumaric acid.

Addition-products of Cinnamic Acid.—Bromhydrocinnamic and iodhydrocinnamic acids are identical with the acids which Glaser obtained (*Liebig's Annalen*, cxlvii, 96) by the action of hydracids on phenyl-lactic acid. Bromhydrocinnamic acid melts at 137—138°, and begins to suffer decomposition at 143°, and if heated for a long time on a paraffin bath, at a temperature not exceeding 150°, in a slow stream of air, it splits up almost quantitatively into hydrobromic and cinnamic acids. No bye-products are formed in this reaction. On boiling with water, two simultaneous reactions take place; one part simply gives off hydrobromic acid, and yields cinnamic acid, while in another part bromine is exchanged for hydroxyl, and phenyl-lactic acid is formed. This is an excellent method for the preparation of the last-named acid.

If bromhydrocinnamic acid is treated with ten times its weight of water (to keep down the heat of the reaction), and sodium carbonate is added to alkaline reaction, a colourless oil collects on the surface, which is pure styrolene. From the alkaline liquid also hydrochloric acid throws down a little cinnamic acid, and from the filtrate a small quantity of phenyllactic acid can be extracted by ether. Iodhydrocinnamic acid acts in a similar manner. The explanation of these reactions is that on bringing bromhydrocinnamic acid into contact with sodium carbonate, the hydrogen-atom of the carboxyl group is exchanged for sodium; then the sodium salt suffers an intramolecular change, in consequence of the affinity of the bromine-atom for the sodium-atom; sodium bromide is formed, and the combining unit of the one oxygen-atom which is set free loosens the carbon-atom of the carboxyl group from the chain. The following equation represents the change:—



$$C_6H_5{-}CH_2{-}CH{<}\begin{matrix}Br\\CO{-}ONa\end{matrix} = C_6H_5{-}CH_2{-}CH + NaBr + CO_2.$$

Styrolene must therefore be regarded as being in reality an unsaturated hydrocarbon.

It is remarkable that the bromine addition-product of cinnamic acid is relatively more stable; on boiling with water it is decomposed into bromostyrolene and phenyllactic acid; but when treated with sodium carbonate, it is converted into a sodium salt, which is easily soluble in water, very slightly so in excess of sodium carbonate, but in the latter case, after standing in the liquid for some days, it becomes easily soluble in water. The formation of methylacrylic acid from the addition products of citraconic acid, probably takes place only when the halogen-atom and the carboxyl-group are in combination with the same carbon atom.

On Teracrylic Acid, a new acid belonging to the Acrylic Series.—Terpenylic acid (see this Journal, 1876, i, 921) splits up on heating into carbon dioxide, and a monobasic acid homologous with pyroterebic acid, for which the name teracrylic acid is proposed. Only about 15 per cent. of the weight of terpenylic acid is thus converted into the new acid. Teracrylic acid may be obtained pure by dissolving the distillate in sodium carbonate or caustic soda, removing the insoluble oil, saturating the clear aqueous solution with dilute sulphuric acid, and distilling. This acid consists of a colourless liquid, with a peculiar odour. It boils at 216—218°; is slightly soluble in water. Its formula is $C_7H_{12}O_2$. The *calcium salt*, $(C_7H_{11}O_2)_2Ca + 5H_2O$, is easily soluble in water, and crystallises in long, colourless, transparent needles, which crumble in dry air. The *silver salt*, $C_7H_{11}O_2Ag$, may be crystallised from hot water in small, colourless needles, which turn brown when exposed to light, and begin to lose acid at 100°.

A third acid, which forms very fine crystals, seems to be formed during the oxidation of oil of turpentine. It is very soluble, and remains in the mother-liquor from the terpenylic acid. If this liquid is saturated with calcium carbonate and evaporated, a gummy mass is left, from which alcohol separates a white, pulverulent, calcium salt. This is soluble in hydrochloric acid, and yields to ether an acid which melts at 163°.

Terebene behaves exactly like oil of turpentine on oxidation with nitric acid or potassium bichromate, but the carefully purified terpene of lemon-oil, which boils at 176°, yields also the same oxidation products as oil of turpentine. The terpenylic acid thus obtained was shown to be in every respect identical with that obtained from oil of turpentine.
G. T. A.

Oxidation of an Acid contained in Crude Petroleum. By Carl Hell and E. Medinger (*Deut. Chem. Ges. Ber.*, x, 451—456).—The authors have obtained from crude Wallachian petroleum, an acid boiling between 250° and 260°, to which they assign the formula, $C_{11}H_{20}O_2$. This substance is resolved by oxidation with chromic or nitric acid into acetic acid, and another acid, the silver salt of which contains about 40·5 per cent. of silver. The latter is probably $C_9H_{18}O_2$, or $C_9H_{16}O_2$, but its constitution has not yet been made out.
J. R.

Synthesis by means of Aceto-Acetic Ether. By J. Wislicenus (*Liebig's Annalen*, clxxxvi, 161—228).—Many of the results recorded in this memoir have been previously published in the *Deut. Chem. Ges. Ber.*, and abstracts of these papers have already appeared in this Journal (1874, 883, and 1876, i, 367). The first part of the memoir consists merely of a review of the labours of the different chemists who have worked at the problem of the action of sodium on acetic ether, and on some of the derivatives obtained from the product.

In acting on ethyl aceto-acetate with sodium, it is necessary to use a diluent, as otherwise the separation of ethyl acetosodacetate in the solid state interferes with the reaction. Pure ether was first used for this purpose, but pure benzene was subsequently found to be more convenient. The ethyl-compound should be mixed with from one half to an equal volume of benzene (not 3 times, as formerly stated), and the sodium added at such a rate as to keep the mixture boiling. From quantitative determinations of the amount of sodium used, the reaction was proved to be—

$$2(CH_3.CO.CH_2.CO.OC_2H_5) + Na_2 = 2(CH_3.CO.CHNa.CO.OC_2H_5) + H_2.$$

In no case is ethyl aceto-disodacetate, $CH_3.CO.CNa_2.CO.OC_2H_5$, formed, as Frankland and Duppa supposed.

The product of the action of ethyl iodide on ethyl aceto-ethylsodacetate, $CH_3.CO.CNaC_2H_5.CO.OC_2H_5$, when submitted to fractional distillation, gave ethyl acetodiethylacetate, $CH_3.CO.C.(C_2H_5)_2.CO.OC_2H_5$, whilst the lower fractions consisted of ethyl acetate, butyrate, and diethyl acetate. Pure ethyl acetodiethylacetate boils at 218°, and is not attacked by sodium, even at 100°; all the lower fractions are.

The results obtained show that the molecule of ethyl acetoacetate can only take up one atom of sodium, but that when this sodium is displaced by an alcohol-radicle, a second atom of hydrogen may be displaced by sodium, and this again by a second alcohol-radicle.

The chief action of sodium ethylate on ethyl acetoacetate is to produce ethyl alcohol and ethyl acetosodacetate; at the same time when the mixture was heated in an oil-bath, at 180°, a distillate was obtained, having a powerful odour of ethyl acetate; this ether was isolated by fractional distillation, and also a minute quantity of a body, which formed a crystalline compound with sodium bisulphite, probably acetone. In a similar manner pure ethyl acetosodacetate, when heated by itself, was decomposed, giving rise to acetone and ethyl acetate, whilst the residue contained sodium acetate.

With ethyl acetoethylacetate and sodium ethylate, a parallel reaction takes place, giving chiefly ethyl alcohol and ethyl acetoethylsodacetate, and when heated at 180—200°, ethyl acetate and butyrate, and a residue containing sodium acetate and butyrate. The successive action of sodium ethylate and ethyl iodide on ethyl acetoethylacetate, gives rise, as might be expected, to ethyl acetodiethylacetate; ethyl acetoethylsodacetate being first produced, which is converted into the diethyl compound by the action of the ethyl iodide.

When equal molecules of sodium ethylate and ethyl acetodiethylacetate are heated in the oil-bath, a reaction takes place, and the mixture begins to boil at about 140°, a mobile liquid passing over into the receiver, whilst sodium acetate, sodium diethylacetate, and carbonate remained in the retort. This distillate, when submitted to careful fractioning, yielded ethyl acetate and diethyl acetate, the latter in by far the larger proportions.

These reactions serve to explain the phenomenon observed by Frankland and Duppa, and others.

1. The crude product of the action of sodium on ethyl acetate is a mixture of sodium ethylate and ethyl acetosodacetate, which, when treated with ethyl iodide, yields sodium iodide, ethyl oxide, and ethyl acetoethylacetate.

2. When a certain quantity of the last named product has been formed, it reacts with a portion of the sodium ethylate, forming ethyl acetoethylsodacetate—

$$CH_3.CO.CH(C_2H_5).CO.OC_2H_5 + NaO.C_2H_5 = CH_3.CO.CNaC_2H_5.CO.OC_2H_5 + C_2H_5.HO.$$

3. A part of this ethyl acetoethylsodacetate is converted into acetodiethylacetate, by the action of the ethyl iodide, whilst another part splits up, with formation of ethyl acetate and butyrate, and sodium acetate and butyrate; the ethyl iodide acting on the last two producing ethereal salts.

4. The ethyl acetodiethylacetate is further acted on by the sodium ethylate, giving rise to ethyl acetate and diethylacetate, and also their sodium salts, the latter, as in the former instance, giving rise to ethereal salts by the action of ethyl iodide.

As all these partial reactions are taking place simultaneously, the products, after the separation of the iodine and sodium as sodium iodide, will consist of ethyl acetoethylacetate, acetodiethylacetate, acetate, butyrate (ethylacetate), and diethylacetate, which may be isolated by fractional distillation. In these reactions a resinous substance of uninviting aspect is produced, which probably plays an important part. The author also remarks that, contrary to his former statement, no dehydracetic acid is produced by the decomposition of *pure* ethyl acetoethylacetate, this acid being indeed formed only when the acetoacetate is present.

In the synthesis of new organic compounds by means of ethyl acetoacetate, it is necessary to avoid the complication produced by the presence of sodium ethylate, so that the crude product of the action of sodium on ethyl acetate cannot be employed. This difficulty is overcome by the use of pure ethyl acetoacetate, which is most conveniently prepared by dissolving 10 parts of sodium in 100 of pure ethyl acetate, at a gentle heat; the ethyl aceto-sodacetate is then decomposed by adding 55 parts of 50 per cent. acetic acid, and 50 of water, agitating, and separating the ethereal layer from the aqueous solution of sodium acetate. By fractional distillation, the ethyl acetoacetate may be separated from the acetate; repeated distillation, however, decomposes a portion of the ethyl acetoacetate with formation of dehydracetic acid. As, moreover, ethyl acetosodacetate readily decomposes by elevation of temperature, considerable care is required in carrying out the process, to ensure a successful result.

The substitution-compounds which are obtained from ethyl acetoacetate, $CH_3.CO.CH_2.CO.OC_2H_5$, by displacing the hydrogen atoms in the CH_2 group successively by sodium and by other carbon groups, and having the general formula, $CH_3.CO.CXY.CO.OC_2H_5$, are capable of undergoing various changes.

I. Geuther showed that ethyl acetoacetate, when saponified, yielded alcohol, acetone, and sodium carbonate, according to the equation—

$$CH_3.CO.CH_2.CO.OC_2H_5 + 2NaHO = C_2H_5.OH + CH_3.CO.CH_3 + Na_2CO_3.$$

This reaction the author has found to be general.

$$CH_3.CO.CXY.CO.OC_2H_5 + 2NaHO = C_2H_5.OH + CH_3.CO.CXYH + Na_2CO_3.$$

Another reaction, however, takes place simultaneously—

$$CH_3.CO.CXY.CO.OC_2H_5 + 2NaHO = CH_3.COONa + CXYH.COONa + C_2H_5.OH.$$

The action of sodium ethylate is analogous to that produced by saponification; but, together with the alcohol, a sodium derivative is produced, which gives rise to more or less complicated reactions. It is evident, therefore, that ketones or ketonic acids, monobasic or polybasic acids will be produced according to the nature of the groups X and Y.

II. The author has previously shown (*ibid.*, cxlix, 205) that ethyl acetoacetate, when treated with sodium in presence of water, yields β-oxybutyric acid—

$$CH_3.CO.CH_2.CO.OC_2H_5 + Na_2 + 2H_2O = CH_3.CH(OH).CH_2.COONa + C_2H_5.OH + NaHO,$$

which, when heated, splits up into water, and α-crotonic acid, $CH_3.CH{=}CH.COOH$. In a similar manner the ethylic salts of acetoethylacetic and acetodiethylacetic acids give rise to the α-derivatives of β-oxybutyric acid, $CH_3.CH(OH).CH(C_2H_5).COOH$ and $CH_3.CH(OH).C(C_2H_5)_2.COOH$.

III. By the action of phosphorus pentachloride, substituted chlorocrotonic acids have been obtained, in which, probably, the chlorine can be replaced by hydrogen.

IV. The production of an ethyl diacetosuccinate by the action of iodine on ethyl acetosodacetate, has been noticed in the papers previously abstracted, as well as some examples of the above transformations of substituted ethyl acetoacetates. C. E. G.

Isopentyl (or Amyl) Acetoacetate. By M. CONRAD (*Liebig's Annalen*, clxxxvi, 228—232).—When sodium is added to isopentyl acetate free from amyl alcohol and boiling at 135—137°, a powerful reaction takes place and the metal dissolves. On heating the mixture to about 140°, amyl alcohol and some amyl acetate distil over, whilst the residue in the retort, when decomposed by acetic acid and a little water, yielded an oily layer, which was submitted to fractional distillation. By this means a liquid was obtained boiling at about 223°, which on analysis gave numbers agreeing with the formula for amyl acetoacetate, $CH_3.CO.CH_2.CO.OC_5H_{11}$. Its density at 10° is 0·954, compared with water at 17·5°. The action of sodium on the amyl aceto-acetate, as is the case with the ethyl-compound, takes place more readily in the presence of benzene. The product, amyl acetosodacetate, when treated with ethyl iodide, yields amyl acetoethylacetate, a colourless liquid of pleasant odour, boiling at 233—236°, and having a density of 0·937 at 26°, compared with water at 17·5°. C. E. G.

Halogen Derivatives of Ethyl Acetoacetate. By M. CONRA

(*Liebig's Annalen*, clxxxvi, 232—244).—After referring to Lippmann's experiments on the action of bromine on ethyl aceto-acetate, which gave rise to an addition-product, $C_6H_{10}O_3Br_2$, the author found, on adding bromine to a solution of ethyl aceto-acetate in chloroform, that the halogen at first combined quietly, but that on the further addition of bromine, hydrobromic acid was evolved in abundance. The product, freed from chloroform and from bromine and hydrobromic acid by exposure in a vacuum over quick lime, had the composition of dibromide of ethyl dibromacetoacetate, $C_6H_8Br_4O_3$. It is a yellowish liquid of density 2·320 at 21° compared with water at 17·5°, and cannot be distilled without decomposition.

On passing pure chlorine into ethyl aceto-acetate, it was readily absorbed, whilst hydrochloric acid was evolved in abundance; when the reaction was terminated, the hydrochloric acid and excess of chlorine was expelled by heating at 100°, and the product distilled. A colourless liquid passed over, which on analysis proved to be ethyl acetodichloracetate, $C_6H_8Cl_2O_3$. It has an ethereal odour, boils at 205—207°, and its density at 16° is 1·293 compared with water at 17·5°. The reaction appears to take place very sharply, as no ethyl chloride or carbonic anhydride is evolved, and the increase in weight corresponds almost exactly to that required for the formation of a dichlorinated derivative.

This chlorinated derivative, when heated for a long time with water, or better with dilute hydrochloric acid at 180°, was decomposed, yielding alcohol, carbonic anhydride, and a dichlorinated acetone, $C_3H_4Cl_2O$, boiling at 120°, identical with the unsymmetric dichlorinated acetone of Borsche and Fittig (*Liebig's Annalen*, cxxxiii, 111). It is evident, therefore, that in ethyl acetodichloracetate both the chlorine atoms must be united to the same carbon atom; this is confirmed by the results of the action of potassic hydrate on the ether. The ether was decomposed by the alkaline hydrate in slight excess, sodic carbonate added, and the mixture, after being evaporated to dryness in a vacuum, was suspended in absolute alcohol, and decomposed by dry hydrochloric acid, so as to convert the acids formed into ethereal salts. These were separated by fractional distillation into ethyl acetate and ethyl dichloracetate, $CHCl_2.CO.OC_2H_5$, boiling at 156°, and identical with that which Wallach obtained (*ibid.*, clxxiii, 288) by the action of potassium cyanide on an alcoholic solution of chloral. The potassium salt of the dichloracetic acid was easily obtained in lustrous plates on saponifying the ether with alcoholic potash.

In order to ascertain to which carbon group in the ethyl acetodichloracetate the two chlorine atoms are united, the action of chlorine on ethyl acetoethylacetate was studied: this gave rise to ethyl acetoethylmonochloracetate, $CH_3.CO.CClC_2H_5.CO.OC_2H_5$, which, by the action of dilute hydrochloric acid at 180°, yielded methylmonochloropropyl ketone, $CH_3.CO.CHCl.C_2H_5$. This is a colourless liquid, having an odour similar to that of monochloracetone, and boiling at 130°. It follows, therefore, that the formula of the ethyl acetodichloracetate is $CH_3.CO.CCl_2.CO.OC_2H_5$, and that of the dichloracetone obtained from it $CH_3.CO.CHCl_2$.

Action of Chlorine on Isopentyl or Amyl Acetoacetate and Acetoethyl-

acetate.—The author has also studied the action of chlorine on these isoamyl compounds: the acetoacetate, as in the case of the ethyl salt, gave a dichlorinated derivative, isoamyl acetodichloracetate, $CH_3.CO.CCl_2.CO.OC_5H_{11}$, whilst the acetoethylacetate gave a monochlorinated derivative, the isoamyl acetoethylmonochloracetate, $CH_3.CO.CClC_2H_5.CO.OC_5H_{11}$. They are both colourless liquids of pungent agreeable odour, and heavier than water. C. E. G.

Allylacetic Ether and its Derivatives. By F. ZEIDLER (*Liebig's Annalen*, clxxxvii, 30—47).—Sodium acetolacetic ether and allyl iodide, when heated together, form *allylacetolacetic ether*, $CH_3.CO.CH\left\{\begin{matrix}C_3H_5\\CO.O.C_2H_5\end{matrix}\right.$, which differs from benzoyl- and benzyl-acetolacetic ethers in being capable of distillation, its boiling point being 206°: it mixes with alcohol, ether, and benzene in all proportions, becomes a fine carmine red with ferric chloride, and has the sp. gr. 0·982 at 20°. Boiling baryta-water saponifies it, forming *allylacetone*, $CH_3.CO.CH_2C_3H_5$; this boils at 128—130°, is of sp. gr. 0·834 at 27°, and possesses the vapour-density 3·4 (theory 3·386): it does not form crystals with sodium-hydrogen sulphite, in this respect differing from the isomerides mesityl oxide (b.-p. 131—132°) and dumasin (b.-p. 120—125°), whilst from the third isomeric body known, metacetone (which does not form such a compound), it differs in boiling-point, metacetone boiling at 84—86°. By oxidation, allylacetone should yield acetic and isocrotonic acids; as, however, the latter readily becomes oxidised to oxalic acid (Hemilian), it might be expected that acetic, oxalic, and carbonic acids only would result, which is the case.

When sodium ethylate and 3—4 molecules of allylacetolacetic ether are heated to 150—160° in a cohobating flask for several days, and the contents of the flask then distilled off, there are obtained, by fractional distillation, ethyl acetate boiling at 72—74°, and a liquid boiling at 142—144°, *allylacetate of ethyl*, $C_3H_5.CH_2.CO.O.C_2H_5$; on saponification with alcoholic potash, &c., this forms *allylacetic acid*, $C_3H_5.CH_2.CO.OH$, boiling at 182°, and smelling something like valerianic acid; the potassium and calcium salts of this were formed and crystallised; the copper salt appeared to be strongly basic. By oxidation with nitric acid, *succinic acid* was formed, as might be expected from the formula $CH_2{=}CH{-}CH_2{-}CH_2{-}CO.OH$.

Nascent hydrogen converts allylacetolacetic ether into *α-allyl β-oxybutyric acid*, $CH_3.OH(OH).CH(C_3H_5).CO.OH$, which cannot be distilled unchanged; the barium salt crystallises anhydrous; the zinc salt is that in which the acid acts as a bibasic acid, $C_7H_{10}O_3Zn,H_2O$; the copper salt prepared by precipitation has an analogous composition.

C. R. A. W.

Benzoylacetoacetic Ether By JULIUS BONNÉ (*Liebig's Annalen*, clxxxvii, 1—11).—On heating ethylic acetosodacetate with the equivalent quantity of benzoyl chloride, the following reaction ensues:—

$$CH_3.CO.CHNa.CO.OC_2H_5 + C_6H_5.CO.Cl = NaCl +$$

$$CH_3.CO.CH\left\{\begin{matrix}CO.O.C_2H_5\\CO.C_6H_5\end{matrix}\right. .$$

By treatment with ether the raw product is dissolved out; after purification by solution in alcohol, precipitation by water, and drying in a vacuum, it forms a liquid having a faint but pleasant odour, and a sp. gr. of 1·14 at 21·5°, readily decomposed at higher temperatures. On distillation benzoic ether is produced, and much benzoic acid; nothing else fit for analysis could be obtained. On saponification with alcoholic potash, *methylphenyl ketone*, potassium acetate and carbonate, and alcohol are formed, thus:—

$$CH_3.CO.CH\left\{\begin{array}{l}CO.O.C_2H_5\\CO.C_6H_5\end{array}\right. + 3HOK = CH_3.CO.OK + CH_3.CO.C_6H_5 + CO(OK)_2 + H.O.C_2H_5.$$

A little benzoic acid is, however, produced by a subsidiary reaction, probably:—

$$CH_3.CO.CH\left\{\begin{array}{l}CO.O.C_2H_5\\CO.C_6H_5\end{array}\right. + 3HOK = 2CH_3.CO.OK + C_6H_5.CO.OK + HO.C_2H_5.$$

A similar decomposition is brought about by heating with water to boiling for a few hours, the chief reaction being—

$$CH_3.CO.CH\left\{\begin{array}{l}CO.O.C_2H_5\\CO.C_6H_5\end{array}\right. + 2H_2O = CH_3.CO.OH + CH_3.CO.C_6H_5 + CO_2 + H.O.C_2H_5,$$

whilst a little benzoic acid is also produced by a subsidiary reaction.

C. R. A. W.

Benzylacetoacetic Ether. By F. Ehrlich (*Liebig's Annalen*, clxxxvii, 11—30).—Benzyl acetolacetic ether has been already prepared by Lydia Sesemann, who obtained it, together with dibenzyl-acetolacetic ether, by Frankland and Duppa's process, viz., acting on ethyl acetate with sodium, and treating the product with benzyl chloride. The author first prepared acetolacetic ether by Geuther's process (acting on the product of the action of sodium on acetic ether with glacial acetic acid), treated this (mixed with benzene) with the equivalent quantity of sodium to form sodium acetoacetic ether, and then added the equivalent amount of benzyl chloride. The product could not be distilled; after due purification it had the sp. gr. 1·083 at 18·4°. When saponified by alkalis it breaks up in accordance with the equation—

$$CH_3.CO.CH\left\{\begin{array}{l}CH_2.C_6H_5\\CO.O.C_2H_5\end{array}\right. + 2HOK = HO.C_2H_5 + CO(OK)_2 + CH_3.CO.CH_2.CH_2.C_6H_5,$$

forming alcohol, potassium carbonate, and *methylphenethyl ketone*. This substance boils at 235—236°, has a faint aromatic odour, and great power of refracting light; its specific gravity at 23·5° is 0·989; it readily combines with acid sodium sulphite, forming the compound $C_{10}H_{12}O.HNaSO_3.H_2O$, by means of which it is readily obtained pure.

By oxidation with chromic solution, methylphenethyl ketone breaks up into acetic, benzoic, and carbonic acids:—

$$CH_3.CO.CH_2.CH_2.C_6H_5 + 3O_2 = CH_3.CO.OH + CO_2 + H_2O + C_6H_5.CO.OH.$$

According to Popoff's observations on the oxidation of ketones, the first product of the action should be acetic and phenylpropionic acids; the latter, being very easily oxidised, should then yield carbonic and benzoic acids: no phenylpropionic acid was found in the unaltered state.

A little dibenzylacetic acid is formed during the saponification of benzylacetoacetic ether by alkalis, owing to the occurrence of a subsidiary reaction; this substance melts at 85—86°, as stated by Lydia Sesemann. Possibly, however, this substance was formed from dibenzylacetoacetic ether contained as an impurity in the benzylacetoacetic ether employed. To judge on this point, attempts were made to prepare dibenzylacetoacetic ether by acting on benzylacetoacetic ether with sodium, and then with benzyl chloride; the body was obtained, but in too small quantity to examine thoroughly the products of its saponification; if the action be parallel with that on benzylacetoacetic ether, diphenisopropylmethyl ketone, $CH_3.CO.CH(CH_2{:}C_6H_5)_2$, should result.

Nascent hydrogen converts benzylacetoacetic ether into *alphabenzylbeta-oxybutyric acid*, just as it forms betaoxybutyric acid from acetoacetic ether; the action of sodium amalgam is, however, slower with the benzylated ether. Alphabenzylbetaoxybutyric acid, $CH_3.CH(OH).CH(CH_2C_6H_5).CO.OH$, melts at 152—155°, and volatilises at 100° with aqueous vapour; its barium salt is $(C_{11}H_{13}O_3)_2Ba,2H_2O$; the zinc salt is a basic body, $C_{11}H_{12}O_3.Zn.H_2O$, the acid acting as a bibasic acid in this case.

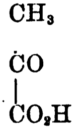
When benzylacetic ether is heated, it breaks up without distilling unchanged; alcohol and methylphenyl ketone are formed; nothing else fit for analysis, however, can be isolated. C. R. A. W.

Ethyl Propionylpropionate. By R. HELLON and A. OPPENHEIM (*Deut. Chem. Ges. Ber.*, x, 860).—The specific gravity of this ether is, 0·9948 (and not 0·9048) at 0°; and 0·9827 at 15°.

C. S.

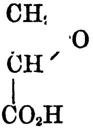
Researches on Ketonic Acids. By J. v. RICHTER (*Deut. Chem. Ges. Ber.*, x, 679—685).—The recent observations of Claisen, and of Hübner and Buchka, pp. 423 and 485 of this volume, on the acid $C_6H_5.CO.CO_2H$, formed from benzoyl cyanide, have induced the author to bring forward some results obtained from a more extended series of experiments on the existence of ketonic acids, and generally on the capability of uniting two carbonyl groups. He thinks that by means of such compounds, a wider field may be opened up by which the theory of the grouping of atoms may be experimentally inquired into, and some idea formed as to which affinities are or are not capable of combination in special cases. Those cases are of especial interest in which there can be perceived a distinct dependence of the capability for combination of multivalent atoms on the nature of the elements or groups already combined with them. Thus, the attachment of two or more carbon-atoms to one carbon-atom is prevented when the former are present as cyanogen-groups (non-existency of the grouping $C(CN)_2.C(CN)_3$; and the single univalent attachment of several oxygen-atoms to a single carbon-atom is determined by the nature of the group already combined with the second affinity of the oxygen or with the carbon, as may be inferred from the existence of the compounds $CH_2(O.C_2H_3O)_2$, $CH(OC_2H_5)_3$, $CCl_3.CH(OH)_2$, and the non-existence of $CH_2(OH)_2$. Especially interesting is the question of the capability of combination of two carbonyl-groups (CO.CO), inasmuch as this capability appears to be distinctly influenced by the nature of the groups already combined with the two carbon-atoms; for example, the question of the existence of acid radicles (diacetyl, dibenzoyl) of ketonic acids, $R.CO.CO_2H$, and of the acids $(CO)_2{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$. One of the first questions in this direction relates to the existence of methylketonic acid, $CH_3.CO.CO_2H$. According to known analogies, such a grouping of atoms would appear to be unstable, but the existence of trichlormethyl-ketonic acid, $CCl_3.CO.CO_2H$, might be predicted, this compound being analogous to phenylketonic acid, $C_6H_5.CO.CO_2.H$, which is a known compound. But since pyruvic acid has lately been regarded as methylketonic acid, further synthetical experiments in this direction appeared to be desirable.

The structure of pyruvic acid may be represented by one of the following formulæ:—



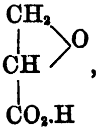
$$\begin{matrix}CH_3\\|\\CO\\|\\CO_2H\end{matrix}$$

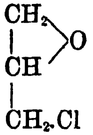
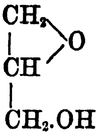
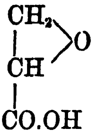
Methyl-ketonic acid.



Etheneoxide-carbonic acid.

Various attempts have been made to prepare methyl-carbonic acid by synthetical processes, but hitherto without success. Thus Henry (*Berichte*, v, 967) prepared the acetylic ether, $CH_3.CO.CH_2.O_2C_2H_3O$, from monochloracetone, but failed to convert it into the corresponding alcohol, $CH_3.CO.CH_2OH$, which should be convertible by oxidation into methyl-ketonic acid. The same chemist (*ibid.*, v, 944), treating chloroxalic ether, $COCl.CO_2.C_2H_5$ with zinc-ethyl, obtained not the expected ether of ethyl-ketonic acid, but Frankland and Duppa's ethylic diethoxalate. Equally unsuccessful was the attempt of Hübner to prepare methyl-ketonic acid from ethyl cyanide, inasmuch as the cyanides of the fatty acids are resolved by water into CNH, and the corresponding acids.

The synthesis of the acid $C_3H_4O_3$ = , was indicated from epichlorhydrin by transformation into the corresponding alcohol, and further oxidation,

To obtain the alcohol, the author attempted first to prepare the acetic ether, using for its production epichlorhydrin and dry sodium acetate in equivalent quantities; finding no reaction take place, he finally heated the materials in a water-bath, using anhydrous alcohol as a diluent. The fluid separated from the resulting sodium chloride gave, when heated in a water-bath, a distillate containing nothing but ethyl acetate and a little alcohol. Several attempts, using other substances as diluents, gave no result. The ether of the epihydrin alcohol is not formed in this reaction in the way expected, but only the ethyl acetate—

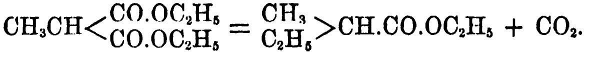
$$C_3H_5OCl + C_2H_3O_2Na + C_2H_5OH = C_3H_5O.OH + C_2H_3O_2.C_2H_5 + NaCl.$$

By frequent fractionation of the oily liquid freed from alcohol and ethyl acetate, a fluid was obtained, showing all the properties of Lourenço's diglycide $(C_3H_6O_2)_2$, which was confirmed by the analysis of the body. The author subsequently became acquainted with the fact that de Gegerfeldt, by acting upon epichlorhydrin with potassium acetate, had obtained the corresponding acetic ether and thence the epihydrin alcohol. As the researches on these synthetical formations have led to no result, the constitution of pyruvic acid can be learned only from the products of its decomposition.

Action of Phosphorus Pentachloride on Pyruvic Acid.—Klimenko obtained an ether after decomposing the product formed by this reaction with alcohol, the greater amount of the ether boiling at 160°, and the analysis indicating it to be dichloropropionic ether. Böttinger has repeated this action under somewhat different circumstances, obtaining an ether which he has concluded to be that of Klimenko. As β-dichloropropinic ether, according to Werigo and Henry, boils at 180°, and α-dichloropropinic ether, according to Beckurts and Otto boils at 158°, the author thinks that there can be no doubt concerning the ether found by Klimenko, and consequently that the structure of pyruvic as methylketonic acid may be regarded as established. He has tried the action of phosphorus pentachloride on pyruvic acid, but has not obtained α-dichloropropinic ether in any quantity. He first took the quantities mentioned by Böttinger, viz., 2 mols. PCl_5, but found that better results were obtained by using 3 mols. PCl_5. On distilling the dried ether, the boiling-point rose from 120—240°, leaving half behind as a thick residue. By repeated fractionation of the amount boiling at 200°, he obtained only a small quantity boiling from 155—160°, containing 38·8 p. c. Cl, dichloropropinic ether requiring 41·5 p. c. Cl. The fraction boiling from 160—165° contained 43·3 p. c. Cl.

Taking also the quantities given by Klimenko, he obtained nearly the same results, finding a liquid boiling at 153—156°, containing only 32·2 and 29·9 p. c. Cl. Using PBr_5, gave no decided results. The author considers, further, that the oxidation of pyruvic acid into acetic and carbonic acids is not decisive of the question under discussion, since acrylic acid also forms acetic acid; also that the change of α-dichloropropinic into pyruvic acid, lately carried out by Otto and Beckurts, is not decisive, since monochloracylic acid would be first formed, from which both acids might be produced. J. M. T.

Decomposition of Ethyl Isosuccinate by Heat. By G. KRESTOWNIKOFF (*Deut. Chem. Ges. Ber.*, x, 409—410).—It was hoped by the above decomposition to obtain methyl-ethyl-acetic acid, with liberation of carbon dioxide:—



$$CH_3CH{<}\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix} = \begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CH.CO.OC_2H_5 + CO_2.$$

It was found, however, that this ether (ethyl succinate) is not decomposable at the temperature at which mercury boils. The silver-salt of the ethyl-isosuccinate is precipitated from a concentrated solution of the ammonium-salt as a heavy granular powder, which, on treatment with water, passes into a loose crystalline mass. If the precipitate be shaken with a great excess of water, a sudden solution takes place, some crystals afterwards separate out, and after a few minutes, the solution becomes converted into a mass of thin, needle-shaped crystals. These crystals are very difficult to dissolve in cold water, but more easy in hot. Byk found that isosuccinic acid is formed if the reaction between chlorpropionic ether and potassium cyanide is conducted in an alcoholic solution. Krestownikoff has, on the contrary, observed that no such formation takes place; in reality, lactic acid, together with another similar acid, being obtained. The latter appeared to be a polymeride of acrylic acid, and is named *paracylic acid.* It crystallises from water in short prisms, melts at 180—182°, and sublimes on further heating in white vapours, having an odour which produces a choking sensation. With ferric chloride it gives a brown precipitate. W. S.

Electrolysis of Ordinary Pyrotartaric Acid. By E. REBOUL and E. BOURGOIN (*Compt. rend.*, lxxxiv, 1231).—When an electric current is passed through a solution of pyrotartaric acid, a slight decomposition takes place, and if the containing vessel be divided into compartments, the acid accumulates at the positive pole, so that after a day or two crystals are deposited on the platinum. The slight decomposition which occurs takes place according to the equation—

$$C_5H_8O_4 = \underset{\text{Positive pole.}}{(C_5H_6O_3 + O)} + \underset{\text{Neg. pole.}}{H_2};$$

and at the positive pole itself $(C_5H_6O_3 + O) + H_2O = C_5H_8O_4 + O$; small quantities of CO_2 and CO are also disengaged.

A concentrated neutral solution of potassium pyrotartrate gives a deposit, in the positive compartment, of acid potassium pyrotartrate, and, subsequently, of free pyrotartaric acid. The same action takes place in presence of free alkali, but it is attended with a greater evolution of gas, the percentage composition of which is CO_2 = 23·7, CO = 35·8, O = 40·5. After two days the positive pole becomes covered with crystals of potassium pyrotartrate. Attempts to procure propylene by the electrolysis of more or less alkaline and concentrated solutions of potassium pyrotartrate were not successful, the only gases evolved being carbonic acid, carbonic oxide, and oxygen.

C. W. W.

Transformation of Ordinary Pyrotartaric Acid into Tribromethylene Hydrobromide. By E. Bourgoin (*Compt. rend.*, lxxxiv, 776—779).—A mixture of ordinary pyrotartaric acid, bromine, and water was heated in a sealed tube for 26 hours at 132°. The chief product of the reaction was an odorous, colourless liquid of density 2·93, which gave off irritating vapours. Its composition corresponds with the formula $C_2H_2Br_4$, which also represents three known compounds, namely, the dibromated ethylene dibromide, with which the present compound is probably identical; the perbromide of acetylene; and the hydride of tetrabromated ethylene. R. R.

Conversion of Ordinary Pyrotartaric Acid into Hydrobromide of Tribromethene. By E. Bourgoin (*Bull. Soc. Chim.* [2], xxvii, 395—397).—The pyrotartaric acid, instead of being purified by the ordinary method with animal charcoal or alcohol, was diluted with water to separate some empyreumatic liquid, and then concentrated at once on the water-bath. The crystals were removed, and the mother-liquor neutralised with sodium carbonate, evaporated, and the sodium salt thrown down with alcohol.

A mixture of 6·5 grams of pyrotartaric acid, 10 c.c. of bromine, and 50 c.c. of water was heated to 130—132° in a sealed tube; the bromine was absorbed in 36 hours, and at 152° in 15 hours. Carbonic anhydride escaped when the tubes were opened, and an oil, with an ethereal smell, sweetish pungent taste, exciting the eyes to tears, was formed. Its specific gravity is 2·93°; it distils at about 200° with partial decomposition. Its formula is $C_2H_2Br_4$. It freezes at −17°, and differs thus from acetylene perbromide, which remains liquid even at −20°. It is attacked by nitric acid, with liberation of hydrochloric acid; and with alcoholic potash a liquid hydrocarbon is formed which absorbs bromine to form the bromide of tribromethene. Three bodies are thus known, all of which have the formula $C_2H_2Br_4$. Acetylene perbromide; the substance described by the author; and tetrabromethene hydride fusing at 54·5°. W. R.

Dry Distillation of Glyceric Acid. By C. Böttinger (*Deut. Chem. Ges. Ber.*, x, 266—269).—The author has obtained, by distilling glyceric acid in a retort over an open flame, and treating the distillate with hydrogen sulphide, a substance which crystallises in beautiful large colourless laminæ melting at 83°. Its composition agrees with the formula $C_8H_6O_4.2H_2O$, and that of its barium salt with the formula $C_8H_4BaO_4.3H_2O$. It is being further examined. J. R.

Furfurol. By A. Baeyer (*Deut. Chem. Ges. Ber.*, x, 355—358).—The author has already shown, when treating of the condensation-products of the aldehydes with the phenols, that furfurol furnishes with resorcin and pyrogallic acid green substances, which resemble the colouring matters of chlorophyll. The question next arising was, "Is the formation of the green colour accompanying the furfurol-phenol condensation, dependent upon the presence of phenol or not?" Pure furfurol is unaltered by concentrated hydrochloric acid, but a blue colour arises on addition of a phenol, which after dilution with alcohol turns permanently green. According to all experience with the aldehyde condensations, a simple condensation-product between furfurol and a phenol cannot, in all probability, be a coloured body. Taking the simplest observed case, 1 furfurol combined with 1 phenol, the following group is obtained:—

$$C\left\{\begin{array}{l} H \\ OH \\ C_4H_3O \\ C_6H_4(OH) \end{array}\right.$$

and from this, by further condensation or decomposition, the green body must arise. This hypothetical group is a phenol-substituted furfur-alcohol, and furfur-alcohol actually gives a green colour with hydrochloric acid. This alcohol is obtained by the action of sodium-amalgam on an aqueous solution of furfurol slightly acidified with acetic acid. By extraction with ether a syrup is obtained, gradually drying in the exsiccator to a colourless varnish. This is the alcohol, and on moistening it with hydrochloric acid it turns green.

While combating the above-mentioned difficulties, the attention of the author was drawn to Perkins's cinnamic acid reaction, and by its means certain most remarkable results were obtained.

Furfur-acrylic acid, $C_4H_3O—CH{=}CH—CO.OH$.—One part of furfurol was heated to boiling with two parts of sodium acetate and four parts of acetic anhydride, for eight hours. The solution solidified on cooling to a crystalline mass, which dissolved almost completely in a warm solution of soda. Acids throw down a precipitate consisting of large yellow needles, nearly equalling in quantity the furfurol employed. Purified from animal charcoal and recrystallised, it was obtained in long, thin, colourless needles. The formation of the acid completely corresponds with that of cinnamic acid from bitter almond-oil and acetic anhydride.

$$\underset{\text{Furfurol.}}{C_4H_3O—CO—H} + \underset{\text{Acetic acid.}}{CH_3—CO—OH} = \underset{\text{Furfur-acrylic acid.}}{C_4H_3O—CH{=}CH—CO—OH} + H_2O.$$

If the group C_4H_3O be termed "Furfur," then the new body is *furfur-acrylic acid*. This acid, isomeric with salicylic acid, smells of cinnamon, melts at 135°, and is easily volatile in vapour of water, without decomposition. It dissolves with difficulty in cold water (about 500 parts), more easily in hot water, and crystallises immediately on cooling.

Furfur-acrylic acid is dissolved by concentrated hydrochloric acid with green coloration, which is tolerably stable. Concentrated sulphuric acid gives also a green condensation-product. Treated with sodium-amalgam in aqueous solution, furfur-acrylic acid yields:—

Furfuropropionic acid, $C_4H_3O—CH_2—CH_2—CO.OH$.—This acid is far more soluble in water. Extracted by ether from its aqueous solution, it remains on evaporation as a colourless crystalline mass, melting at 50—51°, and possessing in a more intense degree the peculiar odour of furfur-acrylic acid.

Furfuropropionic acid is coloured yellow by hydrochloric acid, and when warmed with that acid yields a reddish-yellow solution, which contains a new non-volatile acid now under investigation.

W. S.

Formation of the Benzene Hydrocarbons by Dry Distillation. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, x, 853—855).—The author has found that coal-tar naphtha contains orthoxylene as well as the meta- and para- modifications, and shows by graphic formulæ, that by the condensation of acetylene and allylene, the seven benzene-hydrocarbons existing in tar, and only these (but not the 1, 2, 3 trimethyl-benzene) can be formed. C. S.

Hydrogenisation of Benzene and its Homologues. By F. WREDEN (*Liebig's Annalen.*, clxxxvii, 153—167).—Experiments on hexhydroisoxylene (prepared from isoxylene and camphoric acid), and on the hexhydro-derivatives of toluene, benzene, and cymene, lead to the conclusion that the hydrocarbons of the benzene series cannot take up more than six atoms of hydrogen, and that a direct transition from benzene and its homologues to the homologous members of the methane series with an equal number of carbon atoms in the molecule is not possible. The existence of a series of homologous hydrocarbons of the general formula, $C_6H_{12-m}R_m$ must be granted, which are closely connected in properties (stability, incapability of direct addition, &c.) with the homologous members of the methane series, and contain a closed ring, C_6H_{12}, in the molecule. As yet only the first five members of the series are known, viz.:—

	Boiling point.	Spec. gr. (0°).		
C_6H_{12} ..	69°	0·76		
C_7H_{14} ..	97	0·772	0·758 (20°)	water at 0° = 1.
C_8H_{16} ..	118	0·781	0·765 (20°)	
C_9H_{18} ..	135 to 138	(0·79)		
$C_{10}H_{20}$ ..	153 to 158	0·802	0·788 (23°)	

The regularity of increase in boiling point and specific gravity is noticeable: the difference CH_2 corresponds with a difference of 0·01 in specific gravity.

Like the homologues of methane, these hydrocarbons strongly resist the action of oxidising agents; energetic reactions cause a splitting up of the molecule, carbon dioxide and water being the chief products. (The aromatic tetrahydro-hydrocarbons on the other hand, yield on oxidation aromatic acids with the same number of carbon atoms.) These bodies are distinguished as aromatic hydrocarbons by their mode of origin, and by their transition into the nitro-derivatives of benzene and its homologues; hexhydrobenzene, for instance, is converted by fuming nitric acid into nitrobenzene, and so on. At the same time the added hydrogen is in a state of more intimate lateral connection than in the case of benzene. The capacity of combining with hydrogen also seems to increase in the benzene homologues with the number of methyl groups, probably through the increasing number of lateral bonds. According to Baeyer, the stability of the aromatic hydroacids increases with the number of carboxyl group. The relatively high specific gravity of the hydro-hydrocarbons in question, as compared not only with the homologues of methane, but also with the isomeric olefines, is not without meaning. The same remark applies to tetrahydroisoxylene in relation to the isomerides, C_nH_{2n-2} of the fatty acid series. The higher specific gravity seems to be determined by the closer union of the carbon-atoms to form the closed benzene ring.

G. T. A.

Note.—The author proposes a vowel nomenclature for these aromatic hydro-hydrocarbons, such as—

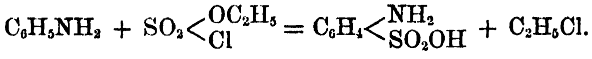
C_6H_{12}	benz*a*l	C_7H_{14}	tolu*a*l
C_6H_{10}	benz*e*l	C_7H_{12}	tolu*e*l
C_6H_8	benz*i*l	C_7H_{10}	tolu*i*l
C_6H_6	benz*o*l	C_7H_8	tolu*o*l, etc.—G. T. A.

Tetrahydroisoxylene and the Constitution of Camphoric Acid. By F. WREDEN (*Liebig's Annalen*, clxxxvii, 168—177).—Under the action of hydrochloric or hydriodic acid, camphoric acid yields a hydrocarbon, C_8H_{14}, with or without admixture of a second one, C_8H_{16}. The first of these exists in two modifications, boiling at 105° and 119° respectively. When treated with chromic acid mixture, the modification boiling at 119° is partially reduced, with evolution of carbon dioxide. A white precipitate is formed in the liquid, from which two calcium salts may be obtained, differing in solubility. The silver salt, corresponding with the more easily soluble calcium salt, when heated in the dry state, swells up like mercury sulphocyanate, and easily explodes. The free acid prepared from the pure calcium salt agrees in properties with isophthalic acid. The less soluble calcium salt yields terephthalic acid. No other fixed products of oxidation were obtained. Two salts were also contained in the volatile part of the oxidation-products, the less easily soluble of which was sodium acetate. The acid prepared from the more soluble salt agreed in properties with isotoluic acid (from isoxylene). Since the hydrocarbon, C_8H_{14} (boiling at 119°), yields on oxidation the same products as isoxylol, it might be expected to consist of tetrahydroisoxylene. This view was confirmed by further experiments. Since the isomeric camphoric acids are shown to be the dicarbo-acids of two isomeric hydrocarbons, viz., tetrahydroisoxylene and the hydrocarbon, C_8H_{14}, boiling at 105°, the ordinary right-handed acid corresponds in all probability with the second of these; the inactive modification, on the other hand, must be regarded as the dicarbo acid of tetrahydroisoxylene, $C_6H_8(CH_3)_2(CO_2H)_2$. G. T. A.

Presence of Benzene in Coal-gas. By M. BERTHELOT (*Compt. rend.*, lxxxiv, 570—576).—The presence of benzene in coal-gas, as mentioned last year (*Chem. Soc. Journ.*, 1876, ii, 183) has been verified by the action of fuming nitric acid upon the gas, and the subsequent reactions of the nitrobenzene formed. It is also found that nitric acid does not act upon ethylene in an appreciable manner, so that this method of estimating the quantity of benzene is not vitiated by the presence of ethylene. Experiments show that only traces of benzene and ethylene are soluble in monohydrate of sulphuric acid ($H_2SO_4.H_2O$, sp. gr. 1·781 at 14°), whilst on the other hand propylene and acetylene are completely absorbed, the former in a few moments, the latter in 25 minutes. The illuminating power of gas is due mainly to the presence of benzene, and it would seem that the illuminating power of a flame is not due to the numerical relation of the carbon to the hydrogen, but, as Frankland has shown, to the condensation of these elements in the unit of volume. F. J. L.

Phorone-cumene. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, x, 855—859).—By heating acetone-phorone with a mixture of sand and phosphorus pentoxide, a little acetone and metaxylene, and a large quantity of *pseudo-cumene* (but no mesitylene) are formed. But on using sulphuric acid, a larger yield of acetone is obtained, and *mesitylene* without its isomeride is produced. C. S.

Action of Sulphuryl Chloride and Ethylsulphuric Chloride on Aniline. By LUDWIG WENGHÖFFER (*Deut. Chem. Ges. Ber.*, x, 441—445).—When ethylsulphuric chloride is dropped into aniline, a violent reaction takes place, resulting in the formation of ethyl chloride and sulphanilic acid. The reaction may be represented thus:—



$$C_6H_5NH_2 + SO_2<\begin{matrix}OC_2H_5\\Cl\end{matrix} = C_6H_4<\begin{matrix}NH_2\\SO_2OH\end{matrix} + C_2H_5Cl.$$

Sulphuryl chloride reacts with acetanilide to form a substance which crystallises from ether, melts at 121°, and gives on analysis numbers agreeing with the formula, $C_8H_7NSO_3$. At the same time hydrogen chloride is set free.

Ethylsulphuric chloride acts upon acetanilide, to form a body agreeing in composition with the formula, $C_{16}H_{16}N_2SO_4$, and crystallising from ether in silky needles.

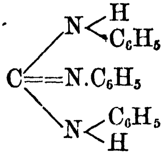
These products are being further examined. J. R.

Behaviour of Aniline-derivatives when passed through Red-hot Tubes. (*Deut. Chem. Ges. Ber.*, x, 474—477).—Dimethylaniline passed through a tube filled with broken glass, and heated to low redness, yields chiefly benzonitril, together with benzene, ammonia, and hydrogen cyanide.

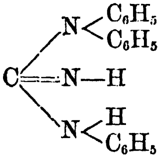
Acetanilide passed slowly through a tube heated to bright redness, yields diphenylcarbamide, with small quantities of benzene, hydrogen cyanide, and aniline. J. R.

Carbotriphenyltriamine. By W. WEITH (*Deut. Chem. Ges. Ber.*, x, 358—362).—From guanidine three triphenylated derivatives are obtainable, viz.:—

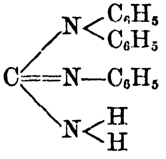
I.



II.



III.



β-triphenylguanidine prepared by Weith and Schröder by the action of cyananilide on diphenylamine, is constituted according to II. α-triphenylguanidine, obtained from diphenylsulphurea and diphenylurea, to I. But the latter constitution ought to belong to the carbotriphenyltriamine which Hofmann obtained by the action of carbon tetrachloride, $C.Cl_4$ on aniline. However, it appeared very possible that under experimental conditions (thirty hours' heating to 170—180°), a shifting of the phenyl groups may have taken place, and thus a compound of formulæ II or III have been formed.

This feeling of doubt occasioned the following research:—

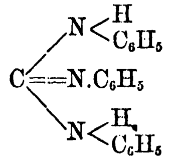
Carbotriphenyltriamine was prepared; its melting point was 195° (α-triphenyltriamine melts at 143°). It dissolved more easily in hydrochloric acid than in water. (The opposite is the case with α-triphenylguanidine.) Its aqueous solution is neutral (α-triphenylguanidine hydrochloride has an alkaline reaction).

Action of Hydrochloric Acid, Potash, and Concentrated Sulphuric Acid on Carbotriphenyltriamine.—By the decomposing action of the above reagents on carbotriphenyltriamine and α-triphenylguanidine respectively, identical products are formed, but as already seen, the physical properties of these two bodies are different. This being the case, it was expected that one of the bases could be converted into the other. Many endeavours in this direction have nevertheless proved fruitless, whether with one or other of the isomeric bases.

Behaviour of Carbotriphenyltrimine on Distillation.—This distillation was undertaken in the hope that α-triphenylguanidine might be formed, or at least be uniformly split up, and thus demonstrate the polymerism of the two bodies.

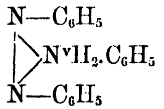
Whilst, however, α-triphenylguanidine when heated, easily decomposes into aniline and carbodiphenylimide (the two on cooling reuniting to the original body), in the case of carbotriphenyltriamine, decomposition begins at 200°, and besides unaltered substance, aniline, ammonia, hydrocyanic acid, diphenylamine and benzonitril are obtained. Neither α-triphenylguanidine nor carbodiphenylimide was found, though most carefully sought for. Thus carbotriphenyltriamine, as regards its behaviour when heated, resembles diphenylguanidine, furnishing similar products.

Carbotriphenyltriamine is considered to be no other than symmetric phenylated guanidine—



Carbotriphenyltriamine.

The fact of the dissociation of α-triphenylguanidine into aniline and carbodiphenylimide suggests a new formula for the α-triphenylguanidine, which is not inconsistent with any of the known reactions of the same; this is—



α-Triphenylguanidine.

W. S.

Phosphophenylic Ether. By H. Köhler and A. Michaelis (*Deut. Chem. Ges. Ber.*, x, 816—818).—Phosphophenyl chloride dissolves, with evolution of heat, in alcohol, producing phosphophenylous acid, which is identical with that produced by the action of water on phosphophenyl chloride; but at the same time an acid ether, $C_6H_5P{\genfrac{}{}{0pt}{}{OH}{OC_2H_5}}$, is produced, which is also identical with that produced by the action of water on phosphenylic ether, and yields an unstable hydrate with water, combining also with water to form phosphenylous acid. Phosphenylic ether may also be obtained by acting on dry sodium alcoholate with phosphophenyl chloride; the substance thus obtained is soluble in ether, distils at 235°, has a sp. gr. 1·032 at 16°, and the composition, $C_6H_5P{\genfrac{}{}{0pt}{}{OC_2H_5}{OC_2H_5}}$. E. W. P.

Isophosphophenylsulphide. By H. Köhler and A. Michaelis (*Deut. Chem. Ges. Ber.*, x, 815—816).—The action of dry sulphuretted hydrogen on hot phosphophenyl chloride gives rise to a yellowish oil, which dissolves in hot ether, forming a solution, which on cooling deposits white crystals, the filtrate leaving a thick liquid on evaporation of the ether. This thick liquid, which has a disagreeable odour, is isomeric with the compound C_6H_3PS produced by the action of sulphur on phenyl-phosphine. This substance is moreover a diphenyl compound, for by the action of nitric acid, diphenylphosphinic, and phosphoric acids are produced, in place of phosphenylic acid. A molecular change having thus far taken place, its constitution must be represented by the double formula, $(C_5H_5)_2P—S—PS$, and it may be regarded as phosphorus trisulphide, PS — S — PS, in which one sulphur-atom is replaced by two phenyl groups.

The white crystals above referred to are odourless, and remain unaltered by water, melting at 192—193°. They are dissolved by nitric acid, diphenylphosphinic acid being produced. The analyses point to the formula, $(C_6H_5)_4P_2S_3$. E. W. P.

Phenylphosphine and Phosphobenzene. By H. KÖHLER and A. MICHAELIS (*Deut. Chem. Ges. Ber.*, x, 807—814).—Phenylphosphine is produced by the action of alcohol on iodophenylphosphine hydriodide—

$$3(C_6H_5PI_2.HI) + 9(C_2H_5.HO) = C_6H_5.PH_2 + 2C_6H_5PO(OH)_2 + 3H_2O + 9C_2H_5I,$$

phosphenylous acid being also produced—

$$C_6H_5PI_2.HI + 3C_2H_5,OH = C_6H_5PO_2H_2 + H_2O + 3C_2H_5I,$$

and this latter reaction absorbing the larger portion of the iodide. The phosphenylous acid thus produced decomposes when heated into phosphenylic acid and phenylphosphine. But phosphenylous acids are best prepared by decomposing phosphenyl chloride with ordinary alcohol in an atmosphere of carbonic anhydride. The residue, after distilling off the alcohol, yields above 250° a mixture of water, benzene, and phenylphosphine: after drying the phenylphosphine and benzene thus obtained, the phenylphosphine distils at 160—161°, in quantity equal to about 14 per cent. of the chloride employed. The reaction therefore takes place according to the equation—

$$3C_6H_5PO_2H_2 = 2C_6H_5PO_3H_2 + C_6H_5PH_2,$$

the benzene and water being produced by decomposition of phosphenylic acid, which decomposes into water and pyrophosphenylic acid, and at higher temperatures into benzene and metaphosphoric acid. The residue after distillation consists of pyrophosphenylic acid, together with a little metaphosphoric acid, which on exposure to the air changes to phosphenylic acid. Phenylphosphine thus obtained is a colourless liquid, of a pungent odour and high refractive power, boiling at 160—161°, and having a specific gravity of 1·001 at 15°. It oxidises rapidly in air, is almost insoluble in concentrated acids, but is rapidly oxidised by warm nitric acid.

Phenylphosphonium iodide, $C_6H_5PH_3I$, is produced by direct combination of phenylphosphine with dry HI gas. It forms white needles which, by heating in an indifferent gas, or by contact with water, are resolved into hydriodic acid and phenylphosphine. The phenylphosphine is but slightly soluble in concentrated hydrochloric acid, but the solution mixed with platinum chloride yields phenylphosphonium platiniochloride, $(C_6H_5PH_3Cl)_2PtCl_4$.

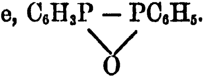
Phenylphosphine and oxygen produce by combination phosphenylous acid $(C_6H_5PO_2H_2)$.

Phenylphosphine and sulphur likewise combine, forming phenylphosphine sulphide $(C_6H_5PH_2S)$ as a thick liquid, soluble in ether, which by continued heating breaks up into isophosphophenyl sulphide, phenylphosphine, and sulphuretted hydrogen—

$$2C_6H_5PSH_2 = C_6H_5PS + C_6H_5PH_2 + H_2S.$$

By the action of sulphur on phenylphosphine, a crystalline substance insoluble in ether, is also produced, which appears to be $(C_6H_5P)_3S$. It melts at 138°, is also soluble in hot nitric acid, and does not separate on cooling.

Phosphobenzene or Diphosphophenyl ($C_6H_5P - PC_6H_5$) is prepared by adding 16 grams of phosphenyl chloride in drops to 20 grams of phenylphosphine contained in a retort, through which passes a stream of dry hydrogen, and fitted with a reversed condenser: at the termination of the reaction, which must be aided by slight heating to remove all traces of hydrochloric acid, the resulting mass is treated with water and with ether free from alcohol. The residue then consists of diphosphophenyl ($C_6H_5PH_2 + C_6H_5PCl_2 = C_6H_5P—PC_6H_5 + 2HCl$). It appears then as a yellowish powder, insoluble in hot water, alcohol, and ether; on exposure to air, it is oxidised to diphosphophenyl oxide,



$C_6H_3P - PC_6H_5$, with O bridging both P atoms.

Chlorine attacks phosphobenzene with violence, producing a liquid which distils at 220—222° (phosphenyl chloride). Oxyphosphobenzene likewise yields with chlorine phosphophenyl chloride and phosphenyl oxychloride $(C_6H_5P)_2O + 2Cl_2 = C_6H_5PCl_2 + C_6H_5PCl_2O$. Dilute nitric acid produces phosphophenylous acid, whereas the concentrated acid yields phosphophenylic acid ($C_6H_5PO_3H_2$). By the action of concentrated hydrochloric acid, phenylphosphine and phosphophenylous acid are formed; in this case probably the chloride is first produced. Neither dilute sulphuric acid, nascent hydrogen, nor alkalis have any action on this body, but with concentrated sulphuric acid an evolution of sulphurous oxide takes place. Phosphobenzene melts at 145—150°, and when kept long above its melting point, yields on cooling, a viscous mass instead of a hard crystalline mass. This mass on oxidation yields diphenylphosphinic acid (m. p. 190°), showing that condensation has taken place: $2(C_6H_3P—PC_6H_5) = (C_6H_5)_2P—P(C_6H_5)_2 + P_2$.

Methylphosphophenyl Chloride.—When phosphophenyl chloride acts on dimethylphenylphosphine, the product is not phosphobenzene, as might be expected, but methylphosphophenyl chloride, thus:—

$$C_6H_5PCl_2 + C_6H_5P(CH_3)_2 = 2C_6H_5P{}^{Cl}_{CH_3}.$$

This substance appears as a yellow crystalline mass, resembling phosphorus pentachloride, melting at 160°, fuming in the air.

As a test for phosphophenylous acid, ferric chloride is recommended; this produces a white precipitate, insoluble in cold concentrated hydrochloric acid, but soluble in the hot acid, and separating as a soft horny mass.

E. W. P.

Aromatic Arsenic-compounds. By A. MICHAELIS (*Deut. Chem. Ges. Ber.*, x, 622—627).—Arsenphenyl tetrachloride, $C_6H_5AsCl_4$, solidifies gradually at the common temperature, quickly at 0°, to broad yellow needles melting at 45°; on cooling it remains liquid for a long time. In moist air it is converted into arsenphenyl oxychloride, $C_6H_5AsOCl_2$, and phenylarsinic acid, $C_6H_5AsO(OH)_2$. While the corresponding phosphorus-compound converts organic acids into their chlorides, the arsenic-compound acts on hot acetic acid as follows:—

$$C_6H_5AsCl_4 + C_2H_4O_2 = C_6H_5AsCl_2 + C_2H_3ClO_2 + HCl.$$

It does not act on sulphur dioxide, which phosphenyl tetrachloride converts into thionyl chloride. On heating it, chlorine is given off, and if carbon dioxide be passed through the hot liquid, it is completely resolved into chlorine and the dichloride. On heating it in a sealed tube to 150°, it splits up into arsenic trichloride and chlorobenzene. On adding more than one molecule of bromine to one of arsenphenyl dichloride, the mixture becomes hot, and paradibromobenzene is formed—

$$C_6H_5AsCl_2 + 2Br_2 = C_6H_4Br_2 + AsClBr + BrH.$$

Arsenphenyl oxide, C_6H_5AsO, is obtained by the action of sodium carbonate on the dichloride; it crystallises from alcohol in crusts, smells like aniseed when cold, but when heated becomes very pungent, and affects the mucous membranes of the nose. It is insoluble in water, melts at 120°, and is reconverted by aqueous hydrochloric acid into the dichloride. On heating it above its melting point, it is resolved into arsenic trioxide and a high-boiling liquid, which solidifies on cooling, and consists probably of triphenylarsine.

Bromine acts violently on it, producing arsenphenyl oxybromide and bromobenzene—

$$(1)\quad C_6H_5AsO + Br_2 = C_6H_5AsOBr_2$$
$$(2)\quad C_6H_5AsO + Br_2 = C_6H_5Br + AsOBr$$

Arsenphenyloxychloride, $C_6H_5AsOCl_2$, is formed by the action of water on the tetrachloride, but is more conveniently obtained by the action of chlorine on the oxide, with which it combines very readily. It is a white crystalline body fuming in the air, and melting at about 100°. Water converts it into phenylarsenic acid; on heating it to 120°, it is resolved into arsenic oxychloride and chlorobenzene.

Arsenphenyl dibromide, $C_6H_5AsBr_2$, is obtained by heating the oxide with concentrated hydrobromic acid. It is a pale yellow liquid, having a faint smell, and boiling, but not without decomposition, at 285°. It is not decomposed by water: bromine converts it into bromobenzene and arsenic tribromide.

Diethylphenylarsine, $C_6H_5(C_2H_5)_2As$, is formed by adding a mixture of the dichloride and benzene or ether to zinc-ethyl. It is a refractive liquid, having a faint but unpleasant smell, and boiling at 240°. It absorbs chlorine readily, forming the crystalline compound,

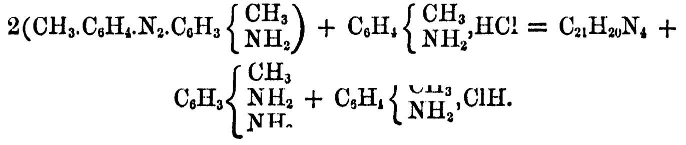
$C_6H_5(C_2H_5)_2AsCl_2$. It also combines with ethyl iodide at 100°, to $C_6H_5(C_2H_5)_3AsI$, crystallising from water in thick needles.

Phenylarsinic anhydride, $C_6H_5AsO_2$, is obtained by heating phenylarsinic acid to 140°; it is an amorphous powder, and has a constitution similar to that of nitrobenzene; on treating it or the corresponding acid with zinc and hydrochloric acid, the smell of an arsine is given off. C. S.

Phosphodiphenyl Chloride and Derivatives. By A. MICHAELIS (*Deut. Chem. Ges. Ber.*, x, 627—628).—This compound $(C_6H_5)_2PCl$, is formed by heating mercury-diphenyl with an excess of phosphenyl chloride for an hour to 220—230°; it is a colourless thick liquid boiling at about 300°; moist air converts it into diphenylphosphinic acid. It readily combines with chlorine, forming the trichloride $(C_6H_5)_2PCl_3$, as a white mass, resembling phosphorus pentachloride. Hot water converts it into diphenylphosphinic acid, $(C_6H_5)_2PO.OH$, which crystallises from concentrated hot nitric acid in needles melting at 190°. It is insoluble in water, sparingly soluble in cold and freely in hot alcohol. C. S.

Behaviour of Phosphenyl Chloride at a High Temperature. By A. BROGLIE (*Deut. Chem. Ges. Ber.*, x, 628).—On heating this compound for some time to 280°, it is resolved into phosphorus trichloride and phosphodiphenyl chloride. When phosphenyl chloride contains free phosphorus, it is purified by heating it to 180—200°, when all will separate out as amorphous phosphorus. C. S.

Action of Amides on Amido-azo-Compounds. By O. N. WITT (*Deut. Chem. Ges. Ber.*, x, 873—877).—When one molecule of an aromatic hydrochloride acts on one molecule of an amido-azo-compound, with formation of sal-ammoniac, *indulins* are formed; but if hydrogen is set free, which reduces a second molecule of the amido-azo-compound, a *saffranine* is produced. In preparing common saffranine, therefore, it is not necessary to oxidise the product of the action of nitrous acid on toluidine, saffranine being in fact formed by heating an alcoholic solution of pure amido-azorthotoluene and orthotoluidine hydrochloride to 150—200°.



$$2\left(CH_3.C_6H_4.N_2.C_6H_3\left\{\begin{matrix}CH_3\\NH_2\end{matrix}\right.\right) + C_6H_4\left\{\begin{matrix}CH_3\\NH_2\end{matrix}\right.,HCl = C_{21}H_{20}N_4 +$$

$$C_6H_3\left\{\begin{matrix}CH_3\\NH_2\\NH_2\end{matrix}\right. + C_6H_4\left\{\begin{matrix}CH_3\\NH_2\end{matrix}\right.,ClH.$$

As the hydrochloride is always regenerated, only a small quantity is required; the diamido-toluidine formed is the para-compound.

C. S.

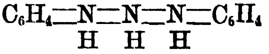
Amid-azo-compounds of the Tolyl-series. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 662—669).—When nitrous acid is passed through orthotoluidine floating on a solution of salt, a thick brown oil is formed, which, after being washed with water and dilute soda, and boiled with hydrochloric acid, yields silvery plates of amido-azotoluene hydrochloride. The free base, $C_{14}H_{15}N_3$, crystallises from alcohol in dark-yellow plates with a fine blue lustre. It is insoluble in water, melts at 100°, and remains liquid on cooling for a long time. Its salts have a yellow colour, are decomposed by water, and its acid solutions are red. $(C_{14}H_{15}N_3ClH)_2PtCl_4$ is sparingly soluble in water, more freely in alcohol, and forms small, thin brown plates. The sulphate is sparingly soluble; on adding silver nitrate to an alcoholic solution of the base, an unstable silver-compound separates out in golden-yellow plates.

When a solution of 2 parts of paratoluidine and 1 part of amyl-nitrite in 8—10 parts of ether is evaporated in a moderately warm place, the corresponding diazamidotoluene is obtained, which, after being washed with alcohol, forms yellow needles. On adding paratoluidine hydrochloride to its alcoholic solution, a reaction takes place without the formation of an amidazo-compound. But orthotoluidine hydrochloride converts it into *orthamidoparazotoluene*, which resembles the ortho-base, only the blue lustre is less brilliant; it melts at 127—128°. The hydrochloride forms vermilion-red needles with a steel-blue lustre. $(C_{14}H_{15}N_3.ClH)_2PtCl_4$ crystallises in needles having a violet lustre; it is not soluble in water and sparingly in alcohol. By the action of aniline hydrochloride on the diazomido-compound, *amidobenzene parazatoluene* is formed, crystallising in long dark-yellow needles, with a brilliant blue lustre, and melting at 147°. The hydrochloride crystallises in rose-coloured, pearly, rhombic plates, and $C_{13}H_{13}N_3ClH)_2PtCl_4$ in small brown needles. On adding silver nitrate to an alcoholic solution of the base, golden-yellow scales of $(C_{13}H_{14}N_3)AgOH$ are precipitated.

The reason why paratoluidine does not form an amidazo-compound, is, probably, that it contains methyl in the paraposition, for amidoazobenzene yields, on reduction, paradiamidobenzene. On the other hand, orthotoluidine does not yield a diazoamido-compound.

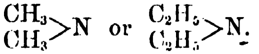
When the pure ortho-base is heated with alcohol and aniline hydrochloride to 160°, a red colour is produced, dissolving in hydrochloric acid with a deep blue colour; the para-ortho-compound yields, under the conditions, a reddish-violet; and the toluene-benzene-compound with orthotoluidine yields a similar colour, and with paratoluidine a bluish-violet. These bodies are undoubtedly isomerides of rosaniline, but are much more like saffranine and magdala-red. Thus on boiling them with zinc-dust, the solution becomes colourless, but colours again rapidly in the air, while leucaniline is only to a small extent converted into rosaniline by oxidising agents. C. S.

Action of Diazo-compounds on Tertiary Amines. By P. GRIESS (*Deut. Chem. Ges. Ber.*, x, 525—530).—The diazo-compounds have long been known to form a peculiar class of compounds with the primary amines. The author has found that they also unite with the secondary amines, *e.g.*, ethylaniline, ethylamidobenzoic acid, &c. The object of the present paper, however, is to show that the diazo-compounds can directly unite with tertiary amines. These new compounds differ from those of the two first-named groups in chemical and physical properties to such an extent that they must be considered to be differently constituted. The best investigated compound of a diazo-body with a primary amine is diazo-amidobenzene, $C_6H_5N{=}N{-}NHC_6H_5$, the rational constitution of which is best expressed by the formula



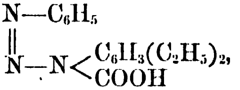
$$\begin{array}{c}C_6H_4{=}N{=}N{=}N{=}C_6H_4\\ H\quad H\quad H\end{array}$$

This body is characterised by the peculiarity of suffering, under certain conditions, an isomeric change, in consequence of which it is converted into a new compound, amidodiphenylimide, $C_6H_5{-}N{=}N{-}C_6H_4(NH_2)$, which must be regarded as the amido-compound of azodibenzene. The diazo-double compounds formed by the help of tertiary amines belong to this type; they are mixed azoamidodibenzenes, which, instead of the group H_2N contain either



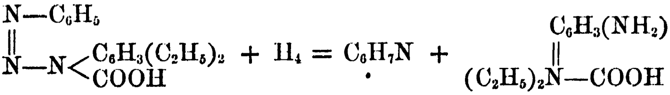
$$\begin{array}{l}CH_3\\ CH_3\end{array}\!>\!N \quad \text{or} \quad \begin{array}{l}C_2H_5\\ C_2H_5\end{array}\!>\!N.$$

Azobenzene-diethylamido-carboxylbenzene,



$$\begin{array}{l}N{-}C_6H_5\\ \|\\ N{-}N\!<\!\begin{array}{l}C_6H_3(C_2H_5)_2,\\ COOH\end{array}\end{array}$$

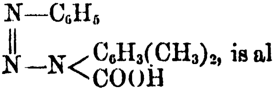
is formed by bringing together concentrated aqueous solutions of one molecule of diazobenzene nitrate and two molecules of metadiethylamidobenzoic acid. It is purified by crystallisation from alcohol. This new compound is soluble in hot alcohol, but almost insoluble in boiling water. When heated gently in a test-tube, it melts into a yellowish-red oil, which is decomposed with explosion at a higher temperature. Its melting-point is 125°. It acts towards bases as a monobasic acid. The *barium salt* $(C_{17}H_{18}N_3O_2)_2Ba$, consists of reddish-yellow short needles. The *silver salt* forms a deep-red imperfectly crystalline precipitate. No compounds could be obtained with acids. It is soluble in mineral acids, but is precipitated from the solutions by addition of water. When the hydrochloric acid solution is heated for some time, decomposition takes place. When treated with reducing agents, it splits up in the following manner:—



$$\begin{array}{l}N{-}C_6H_5\\ \|\\ N{-}N\!<\!\begin{array}{l}C_6H_3(C_2H_5)_2\\ COOH\end{array}\end{array} + H_4 = C_6H_7N + \begin{array}{c}C_6H_3(NH_2)\\ \|\\ (C_2H_5)_2N{-}COOH\end{array}$$

The amidodiethylamidobenzoic acid thus formed, in addition to aniline, crystallises from alcohol in greyish needles or prisms. The same acid may be obtained by nitration of metadiethylamidobenzoic acid and reduction of the nitro-acid formed. Diazobenzene can combine with other tertiary amines, *e.g.*, dimethylamidobenzoic acid, dimethylamine, &c., and as the same property seems to belong to all diazo-compounds, the existence of an almost unlimited number of double-compounds is possible.

Azobenzenedimethylamidocarbonylbenzene,

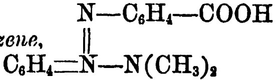


$$\begin{array}{l}N{-}C_6H_5\\ \|\\ N{-}N\!<\!\begin{array}{l}C_6H_3(CH_3)_2,\\ COOH\end{array}\end{array}$$

is also

a monobasic acid formed by the action of diazobenzene on metadiethylamidobenzoic acid. It crystallises in dark blood-red needles.

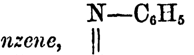
Azocarboxylbenzene-dimethylamidobenzene,



$$\begin{array}{l}\mathrm{N{-}C_6H_4{-}COOH}\\ \|\\ \mathrm{C_6H_4{=}N{-}N(CH_3)_2}\end{array}$$

, is isomeric with the previous acid, and is formed from metadiazobenzoic acid and dimethylamine. It crystallises from alcohol in yellowish-red warty masses.

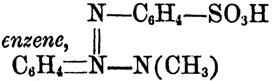
Azobenzene-dimethylamidobenzene,



$$\begin{array}{l}\mathrm{N{-}C_6H_5}\\ \|\\ \mathrm{C_6H_4{=}NN{-}(CH_3)_2}\end{array}$$

, is a base which is formed from diazobenzene and dimethylamine. It crystallises in yellow laminæ which melt at 115°, and volatilise in small quantities without decomposition.

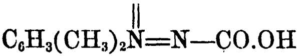
Azosulphoxylbenzene-dimethylamidobenzene,



$$\begin{array}{l}\mathrm{N{-}C_6H_4{-}SO_3H}\\ \|\\ \mathrm{C_6H_4{=}N{-}N(CH_3)}\end{array}$$

, is a tolerably strong acid, formed from diazophenylsulphuric acid and dimethylamine. It is precipitated from a boiling alkaline solution by hydrochloric acid in microscopic needles, which soon change into small violet laminæ.

Metazocarboxylbenzene-metadimethylamidocarboxylbenzene,

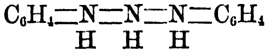


$$\begin{array}{l}\mathrm{N{-}C_6H_4.CO.OH}\\ \|\\ \mathrm{C_6H_3(CH_3)_2N{=}N{-}CO.OH}\end{array}$$

, is an acid formed by the action of metadiazobenzoic acid on metadimethylamidobenzoic acid. It consists of a brownish-red precipitate, which gradually becomes crystalline.

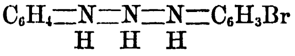
It is worthy of note that all the above compounds are strong colouring matters.

The author adds that the constitution of the compounds of diazobodies with primary and secondary amines is best expressed as in the following instances:—



$$\begin{array}{c}\mathrm{C_6H_4{=}N{=}N{=}N{=}C_6H_4}\\ \mathrm{H\quad H\quad H}\end{array}$$

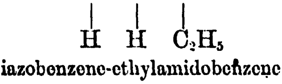
Diazoamidobenzene.



$$\begin{array}{c}\mathrm{C_6H_4{=}N{=}N{=}N{=}C_6H_3Br}\\ \mathrm{H\quad H\quad H}\end{array}$$

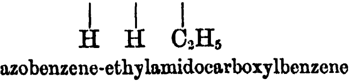
Diazobenzene-amidobromobenzene.

The compounds of diazobenzene with ethylaniline and ethylamidobenzoic acid would be



$$\begin{array}{c}\mathrm{C_6H_4{=}N{=}N{=}N{=}C_6H_4}\\ |\quad\ |\quad\ |\\ \mathrm{H\quad H\quad C_2H_5}\end{array}$$

Diazobenzene-ethylamidobenzene.



$$\begin{array}{c}\mathrm{C_6H_4{=}N{=}N{=}N{=}C_6H_3.COOH}\\ |\quad\ |\quad\ |\\ \mathrm{H\quad H\quad C_2H_5}\end{array}$$

Diazobenzene-ethylamidocarboxylbenzene.

The author is also endeavouring to prepare the not yet known amidopentachlorobenzene, $C_6Cl_5(NH_2)$, in order to see whether it yields diazo-compounds. If this should really be the case, contrary to his expectations, his theory as to the constitution of the latter bodies would be seriously impaired.

G. T. A.

Hydrazine and its Compounds. By H. KOLBE (*J. pract. Chem.*, [2], xiii, 315).—The above name is considered by the author as inexact and inappropriate for the group of substances to which it is applied. Phenylhydrazine, to which Fischer gives the formula $C_6H_5—NH—NH_2$, or $NH<^{NH_2}_{C_6H_5}$, is more correctly written $C_6H_5.H.H_2N\}N$, that is as an ammonia, in which one of the typical hydrogens is replaced by phenyl, and a second by NH_2, and should be called *amidoaniline*. In like manner the hydrazin-compounds are amines, in which one typical hydrogen is replaced by the amido-group, or by a substituted amido-group. Thus the product formed by the action of benzoyl chloride on phenylhydrazine, may be considered as aniline in which one hydrogen atom is replaced by dibenzoyl-amidogen, that is, as—

$$C_6H_5.H.(C_6H_5CO_2)_2N\}N.$$

The formation of phenylhydrazine and its compounds from diazobenzene nitrate presents no difficulty, if we consider the latter as a nitrate of phenylammonium in which three typical hydrogens are replaced by N''', thus, $C_6H_5.N'''\}N^v.O.NO_2$: this substance should then bear the name phenylazo-ammonium nitrate. E. W. P.

Chrysoïdine. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, x, 388—391).—This paper contains a letter of P. Griess, in which he gives the history of this colouring matter; he has also found that it, and similar colours, are formed only by metadiamido-compounds. They may be bases or acids. On reducing chrysoïdine, it yields aniline and triamidobenzene; its constitution is consequently:—

$$C_6H_5N{=}NC_6H_3(NH_2)_2.$$

C. S.

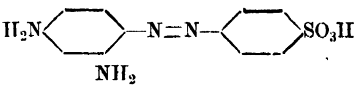
Chrysoïdine. By O. N. WITT (*Deut. Chem. Ges. Ber.*, x, 654—662).—To obtain this base, a 1 per cent. solution of a diazobenzene-salt is mixed with that of metadiamidobenzene containing 10 per cent. The blood-red precipitate is dissolved in boiling water, the solution precipitated at 50° with ammonia of 10 per cent., and the precipitate crystallised from alcohol of 30 per cent. It forms thin yellow needles melting at 117·5°, dissolving very little in cold, and sparingly in boiling water. Alcohol, ether, chloroform, benzene, and aniline dissolve it freely. Its salts dissolve in water with a fine yellow colour, which is changed into a deep red by acids, unstable acid salts being formed. The crystallised salts contain one equivalent of acid, and are obtained by slow cooling in thick, glistening, black octohedrons; but on cooling quickly, or in presence of much acid, long, blood-red, glistening prisms are formed, and if a concentrated solution is cooled down very quickly, it solidifies to a bright red jelly, consisting of microscopic needles. The acetate is a black syrup with a green lustre; the hydrochloride forms with the chlorides of the heavy metals, crystalline double salts. The zinc-compound is soluble in water, but insoluble in a solution of zinc chloride.

When chrysoïdine is heated with methyl iodide, the hydriodide of dimethyl-chrysoïdine is formed; the free base does not crystallise well. On acting on a diazobenzene salt with tetramethyldiamidobenzene, it is converted into tetramethylchrysoïdine, which does not seem to crystallise. All these bodies are colouring matters, the shade of which is the redder the higher the molecular weight. Dibenzylchrysoïdine, which is formed by the action of benzyl chloride on the base, is a beautiful colour.

Diacetylchrysoïdine, $C_6H_5.N_2.C_6H_3(NH.C_2H_3O)_2$, is obtained by boiling the base with acetic anhydride: it crystallises from acetic acid in short thick orange prisms or needles, with a diamond lustre, and showing dichroïsm on certain faces.

When chrysoïdine is treated with tin and hydrochloric acid, it is resolved into aniline and a base giving all the reactions of 1 . 2 . 4 triamidobenzene. On dry distillation it gives off aniline, and a carbonaceous mass containing a reddish-violet body is left behind. By heating chrysoïdine with dilute hydrochloric acid to 150—160°, it yields a red colour and phenol. With amido-compounds it forms colouring matters belonging to the group of the indulins.

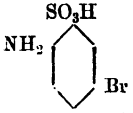
On heating chrysoïdine with sulphuric acid on a water-bath, *chrysoïdinesulphonic acid*, $C_{12}H_{11}N_4SO_3H$, is formed. Its sodium salt crystallises in bronze-coloured scales; the copper-salt is a brownish-red precipitate, which on boiling becomes dark red and crystalline; the ferric salt forms yellowish-brown flakes. The barium salt, $(C_{12}H_{11}N_4SO_3)_2Ba$, crystallises in brilliant brown scales with a golden lustre; on precipitating its solution with hydrochloric acid, a dark brown precipitate of the free acid is formed, which, on boiling, becomes crystalline, and shows a metallic lustre after drying; in concentrated hydrochloric acid it dissolves with a fine red colour. On reducing it with tin and hydrochloric acid and distilling with an alkali, no aniline is obtained, from which it appears that it has the following constitution.



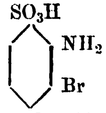
Aniline-yellow, chrysoïdine, and phenylene-brown are members of the same group: their tinctorial power increases with the molecular weight; one part of chrysoïdine imparts to a certain weight of silk the same shade as two of aniline-yellow, while the tinctorial power of phenylene-brown is three times that of the latter. C. S.

Metabromobenzenesulphonic Acid. By ALFRED THOMAS (*Liebig's Annalen*, clxxxvi, 123—134).—Pure benzenesulphonic acid was prepared and neutralized with silver carbonate, and the still warm liquid treated with bromine until no further precipitate of silver bromide was produced; the liquid was then evaporated on the water-bath, neutralised with barium carbonate, and further evaporated; crystals of barium metabromobenzenesulphonate separated, readily purified by animal charcoal; the mother-liquor contained some barium benzenesulphonate. From the barium salt the free acid was prepared by treatment with dilute sulphuric acid; and from this *nitrometabromobenzene sulphonic acid* was obtained by the action of nitric acid: the potassium and ammonium salts are anhydrous, the barium salt is

$\{C_6H_3Br(NO_2)(SO_2)\}_2Ba.3H_2O$: the calcium salt contains $6H_2O$, the lead salt crystallises with $3H_2O$, and the silver salt has $1\frac{1}{2}H_2O$. The chloride of this acid melts at 83°, after crystallisation from ether. By the action of ammonium sulphide this acid forms *amidometabromobenzene sulphonic acid*, of which the potassium salt is anhydrous, whilst the barium salt crystallises with $1\frac{1}{2}H_2O$, and the lead salt with $2H_2O$. By treating this acid with hydriodic acid and amorphous phosphorus at 110°, the bromine is removed, and an *amidobenzenesulphonic acid* formed; from the solubility of this substance it was recognised as the *ortho* acid, whence the nitro-acid is *orthonitrometabromobenzene-sulphonic acid;* moreover, the relative positions of the lateral chains in the orthoamidometabromobenzene-sulphonic acid was found to be :—



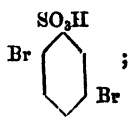
and not



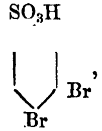
from the circumstance that on conversion into the diazo-derivatives, and treatment with hydrobromic acid, *paradibromobenzene-sulphonic acid* resulted (where the two Br groups are para with respect to one another, one being meta and one ortho with reference to the sulphonyl-group). The potassium salt of this dibrominated acid crystallises with $1H_2O$, whilst the barium salt forms needles containing $1\frac{1}{2}H_2O$, and prisms with $5H_2O$.

When orthonitrometabromobenzene-sulphonic acid is heated to 160° with alcoholic ammonia, the bromine is removed and amidogen substituted for it, forming *orthonitrometamidobenzene-sulphonic acid*, the barium salt of which crystallises with $1\frac{1}{2}H_2O$; a little of a body melting at 151—152° was formed, probably an impure *paranitrobromobenzene*, as it seemed to form parabromaniline on reduction with tin and hydrochloric acid. C. R. A. W.

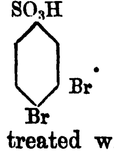
Action of Bromine on Silver Benzenesulphonate and Metabrombenzenesulphonate. By H. LIMPRICHT (*Liebig's Annalen*, clxxxvi, 134).—On adding bromine to the silver salt of pure benzene-sulphonic acid (prepared freshly from silver carbonate) until no more silver bromide separates, treating with barium carbonate, and evaporating, barium metabromobenzene-sulphonate separates in crystals containing $2H_2O$; the silver salt of this acid is anhydrous; the chloride is oily, and the amide crystallises in minute plates, melting at 154°, whence the acid is evidently the *meta* acid. On treating silver metabrombenzene-sulphonate with bromine in the same way, there are formed *bromanil* in small quantity, and some of the dibrominated acid,
SO_3H

Br ; a somewhat larger quantity of the isomeric *paradibromobenzene-sulphonic acid* is formed, having the constitution  ;

the greater portion of the metabromobenzene-sulphonic acid employed, however remains unaltered. These acids were separated, first partially, by mechanically picking out the crystals of the barium salts, and then converting them into chlorides; that of the monobrominated acid, being oily, is readily separated from that of the paradibromo-acid by crystallisation from ether. The latter chloride melts at 71°; by treatment with water at 170° it regenerates the acid, which crystallises with $3H_2O$; the hydrated crystals melt at 99°; when rendered anhydrous the acid melts at 124°. The barium salt crystallises with $1\frac{1}{2}H_2O$ and with $1H_2O$; the potassium salt with $1H_2O$; the calcium salt with $4H_2O$, and the lead salt with $3H_2O$. By treatment with nitric acid *nitrodibromobenzene-sulphonic acid* is formed, the barium salt of which contains $1H_2O$.

The acid isomeric with the paradibromobenzene-sulphonic acid was obtained from the mixture of amides resulting from the action of ammonia on the first crude mixture of chlorides by crystallisation, whereby the amide of the paradibromo-acid first separated, melting at 193°; subsequently crystals melting at 170°, after purification, were obtained; these were heated in sealed tubes to 170° with hydrochloric acid in order to form the acid. The barium salt crystallises with $2H_2O$, the lead salt with $2H_2O$; the chloride is crystallisable, melting at 31°; the amide is difficultly soluble in water, and melts at 170°. That the acid possesses the structure assigned to it, , is shown by the fact that it is obtainable, not only from *meta*-bromobenzene-sulphonic acid, but also from the *para* isomeride (vide next abstract).

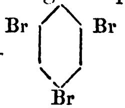
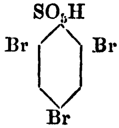
C. R. A. W.

A New Dibromobenzene-sulphonic Acid. By C. Goslich (*Liebig's Annalen*, clxxxvi, 148).—Parabromobenzene-sulphonic acid was prepared by acting on bromobenzene with sulphuric acid; from the silver salt of this a dibrombenzene sulphonic acid was prepared by the action of bromine, a certain amount of the monobrominated acid escaping change. The dibrominated-acid crystallises with $3H_2O$, the hydrated crystals melting at 57—58°; when anhydrous it is so hygroscopic that the melting point cannot be found. The potassium salt is anhydrous, as are the ammonium, calcium, and silver salts; the barium and lead salts crystallise each with $2H_2O$. The chloride melts at 31°, and the amide at 170°, whence the acid is identical with that obtained by Limpricht in small quantity from metabromobenzene sulphonic acid by bromination (vide preceding abstract); wherefore its structure must be .

When treated with nitric acid a *nitrodibrombenzene sulphonic acid* is formed, of which the potassium and ammonium salts crystallise anhydrous, the barium and lead salts with $3H_2O$, and the calcium salt with $4H_2O$ and with $6H_2O$. The chloride of this acid melts at 98—99°, and the amide at 210—211°.

By the action of bromine on the silver salt of the dibrominated acid, small quantities of a *tribrombenzene sulphonic acid* are formed; the barium salt of this crystallises with $3\frac{1}{2}H_2O$: the chloride crystallises from ether, and melts at 120—121°: the amide fuses at 152°.

C. R. A. W.

On a Tribromobenzenesulphonic Acid. By O. Reinke (*Liebig's Annalen*, clxxxvi, 271—290).—The following compounds were prepared from symmetric tribromobenzene:—  (m. p. 118·5°). From this only one sulpho-acid can be formed, viz.,  and it is this which is here described. The tribromobenzene was prepared by the action of nitrous ether on tribromaniline.

The tribromobenzenesulphonic acid was prepared from the tribrombenzene as follows:—The latter was heated in sealed tubes with twice its volume of fuming sulphuric acid in the water-bath for a week. After this the tubes were opened, their contents placed in water, and the resulting liquid was filtered from insoluble matter. In this, much unaltered tribrombenzene was contained, which was recovered by drying and redistillation. The filtered aqueous solution was neutralised with milk of lime, filtered, evaporated, and, after addition of alcohol, the lime was completely precipitated with sulphuric acid. After filtering and distilling off the alcohol, the boiling solution was neutralised with barium carbonate, and the barium tribromobenzenesulphonate was purified by repeated recrystallisations. The yield was not very satisfactory.

Tribromobenzenesulphonic Acid, $C_6H_2Br_3(SO_3H)$.—Prepared by precipitation of the barium-salt with dilute sulphuric acid, and evaporating the filtrate on the water-bath. So prepared it formed a yellowish radiating crystalline mass, consisting of delicate needles and prisms. It is hygroscopic, soluble in water in all proportions, also soluble in alcohol, but not so much so in ether. At 100° it melts, and crystallises on solidifying, on further heating, tribromobenzene sublimes. The aqueous solutions give precipitates with potassium carbonate, barium chloride, and lead acetate. In one preparation an acid was obtained with properties different from those of the above. It crystallised more easily, and formed tolerably large, white, shining, rhombic tables, which were not very soluble in water. The barium salt of this acid contained a different amount of water of crystallisation from that of the preceding. The chlorides of the two acids appeared completely identical; their melting point was 63°. The analysis of this acid led to the formula $C_6H_5Br_3(SO_3H) + 2H_2O$. Theoretically only one tribromosulphobenzenic acid should be obtained from the symmetric tribromobenzene, but here are, apparently, two different acids which have been prepared from it. If a similar placing of the atoms in the molecule be assumed, then the difference can only be accounted for by supposing a different grouping of the molecules, similar to that observed in dimorphous compounds. It is remarkable, however, that the one modification could not be converted into the other. Both compounds possess more stability than is generally observed in bodies possessing the same chemical composition and structure, but different physical properties. The further investigation of this interesting subject could not be further followed up. Almost the whole research was made with the first-named and easily soluble acid.

Potassium Tribromobenzenesulphonate, $C_6H_2Br_3SO_3K + H_2O$.—White microscopic, rhombic tables, pretty easily soluble in hot water.

Ammonium Salt, $C_6H_2Br_3(SO_3.NH_4) + H_2O$.—White rhombic tables, easily soluble in cold water, and still more so in hot.

Barium salt, $(C_6H_2Br_3SO_3)_2Ba + 9H_2O$.—Colourless, or faint reddish-coloured shining plates. Sparingly soluble in cold water, much more easily in hot.

The barium salt of the less soluble acid had the composition $(C_6H_2Br_3SO_3)_2Ba + 2H_2O$.

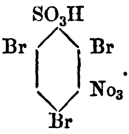
Calcium salt, $(C_6H_2Br_3SO_3)_2Ca + 7H_2O$.—White silky plates; under the microscope these appeared as rhombic tables. Moderately easily soluble in water.

Lead salt, $(C_6H_2Br_3SO_3)_2Pb + 9H_2O$.—White, shining, rhombic plates, very small. Soluble with difficulty in cold, easily in hot water.

Silver salt, $C_6H_2Br_3SO_3Ag + H_2O$.—Yellowish concentrically-grouped needles.

Tribromobenzenesulphochloride, $C_6H_2Br_3SO_2Cl$.—The dried potassium salt, heated with phosphorus pentachloride, is converted into the above chloride, and this may be purified by washing with water and frequent recrystallisation from ether. Colourless, transparent, rhombic tables, very soluble in ether. Melting point 63°.

Tribromobenzenesulphamide, $C_6H_2Br_3SO_2NH_2$.—Prepared by digesting the chloride with concentrated ammonia, and obtained as a yellowish powder after repeated crystallisation from water. Under the microscope it appears to consist of fine needles. It is very difficultly soluble in hot water. It darkens at 210—220° without melting, and is carbonised at a higher temperature, with formation of a white sublimate.

Nitrotribromobenzenesulphonic Acid, 

.—The tribromobenzenesulphonic acid was boiled for an hour with the most concentrated nitric acid; the solution was then evaporated to dryness on the water-bath, and the residue treated with water. A faint yellowish-coloured crystalline residue remained, soluble in alcohol and ether, and melting at 124°. It was probably the nitrotribromobenzene described by Jackson (*Deut. Chem. Ges. Ber.*, viii, 1172). The aqueous solution on evaporation furnished the nitrotribromobenzenesulphonic acid in stellar groups of needles and in quadratic prisms, easily soluble in water, somewhat less so in alcohol, with difficulty in ether. Melts a little above 100°; turns brown and begins to decompose at 160°. The dilute solution gives precipitates with barium chloride and lead acetate.

Potassium Nitrotribromobenzenesulphonate, $C_6H.NO_2Br_3SO_3K$, anhydrous. Easily soluble. Needles arranged in stellar groups and of a faint yellowish colour.

Ammonium salt, $C_6HNO_2Br_3SO_3NH_4$, anhydrous.—Faint yellowish, concentrically grouped needles, easily soluble in water.

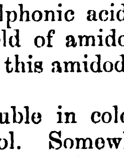
Barium salt, $(C_6H.NO_2Br_3SO_3)_2Ba + 1{\cdot}5H_2O$.—Shining white crystalline powder consisting of minute rhombic tables. With difficulty soluble in cold or hot water.

Calcium salt, $(C_6H.NO_2Br_3SO_3)_2Ca + 2H_2O$,—White, right-angled prisms (microscopic). Easily soluble in water.

Lead salt, $(C_6HNO_2Br_3SO_3)_2Pb + 1{\cdot}5H_2O$.—Microscopic, white, rhombic tables, sparingly soluble in water.

Sulphochloride, $C_6HNO_2Br_3SO_2Cl$.—By heating the potassium salt with phosphorus pentachloride, or by heating the calculated quantity of phosphorus chloride and some phosphorus oxychloride in sealed tubes to 140°. After washing with water, drying, and dissolving in anhydrous ether, a thick oil remains on evaporation. Only once was a solid slightly soluble substance found therein on treating with petroleum ether. This substance was easily dissolved by ether, and it crystallised from the solution in microscopic rhombic prisms and tables, which became brown at 180°, without melting.

Nitrotribromobenzenesulphamide, $C_6HNO_2Br_3SO_2NH_2$.—Prepared by the action of concentrated ammonia on the sulphochloride. It was purified by repeated recrystallisation from water. Faint yellowish powder, consisting of microscopic plates, sparingly soluble in water, easily in alcohol. Turns brown at 210°, without previous fusion.

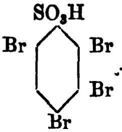
Amidotribromobenzenesulphonic Acid, 

+ H_2O.—Prepared by treating the nitrotribromobenzenesulphonic acid in the cold with tin and hydrochloric acid. If the solution be warm, or the action long-continued, an amidodibromobenzenesulphonic acid is formed. If the solution be too cool, a very small yield of amidotribromo-product is obtained, and hence the formation of this amidodibromo-derivative is very difficult to avoid.

White, silky needles, moderately soluble in cold water, more so in hot. Soluble to some extent in alcohol. Somewhat bitter astringent taste. When heated they blacken above 200°, and burn on platinum-foil without melting. The concentrated solution gives precipitates with potassium carbonate and lead acetate, but none with barium chloride or calcium chloride.

Diazo-compound of the above acid. This was obtained by suspending the finely pulverised acid in alcohol and treating it with nitrous acid. The solution then assumed a yellowish colour, and was converted into a mass of microscopic rhombic tables consisting of the diazo-compound.

Tetrabromobenzenesulphonic Acid,



.—On treating the diazo-compound with boiling hydrobromic acid, nitrogen gas was evolved, and on evaporating on the water-bath, a yellowish crystalline mass remained which, on recrystallising from water, yielded the acid in question in needles and six-sided tables. It is very soluble in water, but less so in alcohol; melts when heated on platinum-foil. Its solution is precipitated by barium chloride.

Potassium salt, $C_6H_2Br_4SO_3K$ (anhydrous).—Silky, microscopic needles or long prisms, easily soluble in water.

Ammonium salt, $C_6HBr_4SO_3NH_4$ (anhydrous).—Prepared from the calcium salt by the action of ammonium carbonate. Faint reddish, shining, rhombic plates. Easily soluble in water.

Barium salt, $(C_6HBr_4SO_3)_2Ba + 1\cdot5H_2O$.—Microscopic rhombic prisms, sparingly soluble in cold and hot water, and separating very slowly from solution.

Calcium Tetrabromobenzenesulphonate, $(C_6HBr_4SO_3)_2Ca + 8H_2O$.—Delicate needles of faint reddish tint; under the microscope rhombic prisms. Very soluble in water.

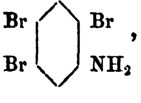
Lead salt, $(C_6HBr_4SO_3)_2Pb + 1\cdot5H_2O$ and $2H_2O$.—Prepared by neutralising the acid with lead carbonate. Microscopic six-sided prisms with $2H_2O$. On evaporation, somewhat larger rhombic prisms were obtained containing $1\cdot5H_2O$.

Sulphochloride, $C_6HBr_4SO_2Cl$.—Colourless or faintly brownish rhombic plates, easily soluble in ether. At 85° it begins to run, and at 91° it is quite fused.

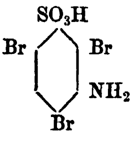
Tetrabromobenzenesulphamide, $C_6HBr_4SO_2NH_2$.—Crystallised from water it forms a white powder; from alcohol, microscopic needles. Sparingly soluble in water, easily in alcohol. It blackens at 250° without previous fusion. Melts on platinum-foil, and burns, giving off white vapours.

The similarity between the tetrabrominated acid prepared by the author and that by Beckurts is pointed out, but it is scarcely possible to assume their identity, as they distinctly differ in some particulars. The investigation of this subject could not be followed up.

Were the two acids identical, the tribromobenzenesulphonic acid chosen at the outset by the author would be identical with that from which Beckurts prepared his tetrabromobenzenesulphonic acid, and from this it would follow that his amidotribromobenzenesulphonic acid has not the structure which he assumes for it, viz.,



, but



Amidodibromobenzenesulphonic Acid, $C_6H_2NH_2Br_2SO_3H$. — Prepared by the prolonged action of tin and hydrochloric acid, with aid of heat, upon nitrotribromobenzenesulphonic acid. It is thus reduced to the above-named amidodibromo-derivative. The reaction is completed in two hours. The tin is removed by sulphuretted hydrogen, the solution evaporated to dryness, and the residue recrystallised from hot water. This acid is probably identical with that first prepared by Berndsen and afterwards by Beckurts (*Liebig's Annalen*, 177, 184, and 181, 213). Anhydrous, white, microscopic, rhombic prisms, soluble with difficulty in hot and cold water and in alcohol. Blackens at 260° without melting.

Potassium salt, $C_6H_2NH_2Br_2SO_3K + H_2O$.—Almost colourless, shining, crystalline powder, consisting of microscopic plates, easily soluble in water.

Ammonium salt, $C_6H_2(NH_2)Br_2(SO_3NH_4)$ (anhydrous).—Faintly reddish needles, very easily soluble in water.

Barium salt, $(C_6H_2NH_2Br_2SO_3)_2Ba + 5H_2O$.—Easily soluble needles. long and united in clusters.

Calcium salt, $(C_6H_2NH_2Br_2SO_3)_2Ca + 5H_2O$.—Faint reddish, microscopic needles, easily soluble in water.

Lead salt, $(C_6H_2NH_2Br_2SO_3)_2Pb$ (anhydrous).—Faint reddish needles, moderately easily soluble in water.

The *diazo-compound* could not be obtained.

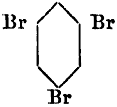
Tribromobenzenesulphonic acid, $C_6H_2Br_3SO_3H$, was prepared by suspending the amidodibromobenzenesulphonic acid in hydrobromic acid and passing nitrous acid through the liquid, heat being applied in the meantime. This was done till all was dissolved, and no more development of gas occurred. On evaporating on the water-bath, the above-named tribromosulpho-acid remained. Silky, shining crystalline powder, consisting of microscopic needles. Soluble in water and in alcohol. The moderately dilute solution gives precipitates with potassium carbonate, barium chloride, and lead acetate.

Potassium salt, $C_6H_2Br_3SO_3K + H_2O$.—Well formed, white, shining rhombic plates and needles. Soluble with difficulty in cold, easily in hot water.

Barium salt, $(C_6H_2Br_3SO_3)_2Ba + 2H_2O$.—Soluble with difficulty in water. By evaporating the solution on the water-bath, white, rhombic, microscopic plates are deposited.

Sulphochloride, $C_6H_2Br_3SO_2Cl$.—Easily formed by the action of phosphorus pentachloride on the potassium salt. It crystallises from ether in rather large colourless needles, concentrically grouped. These appear to be rhombic prisms. Melting point of one chloride, 78°, of another prepared otherwise 84·5°.

Tribromobenzenesulphamide, $C_6H_2Br_3SO_2NH_2$.—By warming the sulphochloride with concentrated ammonia. Separates from the hot aqueous solution as a white powder, appearing under the microscope to consist of long, flat rhombic tables. Very difficult to dissolve in water. Melts at 225° and becomes darker in colour. W. S.

On a Tribromobenzenesulphonic Acid. By PAUL KNUTH (*Liebig's Annalen*, clxxxvi, 290—306).—This tribromobenzenesulphonic acid was prepared, by exchange of NH_2 for H, from the tribromometamidobenzenesulphonic acid described by Berndsen and Beckurts (this Journal, 1876, ii, 304). Tribromometamidobenzenesulphonic acid was converted into the diazo-compound according to Beckurts' method. The conversion of this diazo-compound with absolute alcohol was conducted under pressure. Several hours' boiling were required before the whole was dissolved and the action completed. The clear solution was evaporated on the water-bath, the tribromobenzenesulphonic acid remaining dissolved in water, filtered, and the filtrate precipitated with barium chloride. The barium salt was now purified by repeated crystallisation from hot water with addition of animal charcoal. The acid, $C_6H_2Br_3SO_3H + H_2O$, obtained from this barium salt by decomposition with dilute sulphuric acid, crystallised on long standing in long, transparent, colourless needles, quickly deliquescing in the air, and very soluble in alcohol. The acid obtained from the chloride by heating with water from 120° to 140° formed transparent rhombic tables, likewise easily soluble. The acid thus prepared had not only a different crystalline form, but yielded a barium salt containing a different amount of water of crystallisation. By heating to 100° it melted, and on stronger heating yielded a sublimate of tribromobenzene,  (melting at 118·5), leaving a black tarry residue. From this reaction it is considered probable that this acid is identical with that obtained by Reinke from symmetrical tribromobenzene. However, the salts and other derivatives of the two acids show considerable differences, and hence the author cannot venture to speak with certainty as to this identity.

Potassium salt, $C_6H_2Br_3SO_3K + 3H_2O$.—Shining yellow laminæ, grouped like fern-leaves, and separating into rhombic tables when pressed.

Ammonium salt, $C_6H_2Br_3SO_3NH_4 + H_2O$.—Easily soluble, white rhombic tables.

Barium salt $(C_6H_2Br_3SO_3)_2Ba + 8H_2O$.—Large, shining, yellowish leaves, obtained quite white on treatment with animal charcoal. This salt was proved to be pure, *i.e.*, free from any isomeric salt, by fractional crystallisation and careful examination of the first and last fractions.

From the acid crystallising in rhombic tables, and prepared from the chloride by heating with water, a barium salt was obtained of the following composition:—$(C_6H_2Br_3SO_3)_2Ba + 2H_2O$.—It crystallises in white, rhombic tables.

Calcium salt $(C_6H_2Br_3SO_3)_2Ca + 8H_2O$.—Bright yellow, silky needles.

Lead salt $(C_6H_2Br_3SO_3)_2Pb + 6H_2O$.—Shining, yellowish-white plates.

Silver salt $C_6H_2Br_3SO_3 + H_2O$.—Long needles arranged in clusters, white and easily soluble, quickly blackening when exposed to light. An attempt to obtain a tetrabromobenzenesulphonic acid from the silver salt by addition of bromine-water was unsuccessful.

Sulphochloride, $C_6H_2Br_3SO_2Cl$.—Crystallises from ether in colourless rhombic prisms, melting at 64·5°.

Tribromobenzenesulphamide, $C_6H_2Br_3SO_2NH_2$.—Prepared by the action of concentrated ammonia on the chloride. Crystallises from alcohol in white, silky needles. Soluble with difficulty in hot water, easily in alcohol. It turns brown at 220°, and volatilises with decomposition at 228°.

Nitrotribromobenzenesulphonic Acid, $C_6H(NO_2)Br_3(SO_3H)$.—The dry tribrombenzenesulphonic acid is boiled for some time with concentrated nitric acid in a retort. On evaporation to dryness, and treatment with water, a residue is obtained which crystallises from alcohol and ether in very hard, flat needles of a yellow colour. This body melts between 124° and 125°, and appears to be the nitrotribrombenzene described by Jackson. The aqueous solution leaves the nitrotribrombenzenesulphonic acid in stellate groups of yellowish-white needles, deliquescent in the air, very soluble in alcohol, less so in ether. On heating them in a glass tube, a sublimate is formed of the symmetrical tribrombenzene.

Potassium salt, $C_6HNO_2Br_3SO_3K + 1{\cdot}5H_2O$.—White, shining needles, in radiating groups. Easily soluble in hot water, with difficulty in cold.

Barium salt $(C_6HNO_2Br_3SO_3)_2Ba + 10H_2O$.—Chloride of barium precipitates the solution of the free acid. The precipitate dissolves with difficulty in hot water and separates out slowly in yellow needles in stellar groups. By treatment with animal charcoal these were obtained white.

Calcium salt, $[C_6H(NO_2)Br_3SO_3]_2Ca + 3{\cdot}5H_2O$.—Shining, white, microscopic plates, easily soluble in water.

Sulphochloride, $[C_6H(NO_2)Br_3(SO_2)Cl]$.—Flat rhombic tables, with two flattened corners. They turn brown at 126° and melt at 142°.

Nitrotribromobenzenesulphamide, $[C_6H(NO_2)Br_3SO_2NH_2]$.—Crystallises from alcohol in silky microscopic needles, easily soluble in alcohol, with difficulty in water. Turn brown at 169°, soften at 175°.

Amidotribromobenzenesulphonic Acid, $[C_6H(NH_2)Br_3SO_3H]$.—The nitrotribromobenzenesulphonic acid is not reduced by treatment with ammonium sulphide, but on treating it with tin and hydrochloric acid and warming, the amidodibrominated acid is produced. This action if carried on in the cold however, gives the tribromoamido-acid. Small, white needles, moderately soluble in water.

Potassium salt, $[C_6H(NH_2)Br_3SO_3K] + H_2O$.—Small, white needles, moderately soluble.

Barium salt, $[C_6H(NH_2)Br_3SO_3]_3Ba + 4H_2O$.—Small, white needles, and tables, moderately soluble in water.

The Diazo-compound, obtained by passing nitrous acid through a concentrated alcoholic solution of the amidobenzenesulphonic acid, forms yellow, rhombic, microscopic plates, which swell up when heated on platinum foil. The solution in concentrated hydrobromic acid furnishes a

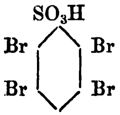
Tetrabromobenzenesulphonic Acid, $C_6HBr_4SO_3H$, which crystallises on evaporation from water, in stellate groups of easily soluble needles.

Potassium salt, $[C_6HBr_4SO_3K]$, (anhydrous).—Small white needles, easily soluble in water.

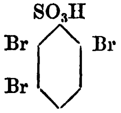
Barium salt, $[C_6HBr_4SO_3]_2Ba + 1{\cdot}5H_2O$.—The solution of the acid gives with barium chloride a precipitate, which was recrystallised from hot water. Faint-reddish needles, with difficulty soluble in water.

Sulphochloride, $C_6HBr_4SO_2Cl$.—The dry potassium salt was heated in sealed tubes to 120° with the calculated quantity of phosphorus pentachloride and some phosphorus oxychloride. The chloride, easily soluble in ether, crystallises therefrom in reddish rhombic plates, melting at 93°.

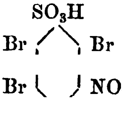
Tetrabromobenzenesulphamide, $C_6HBr_4SO_2NH_2$.—Crystallises from alcohol in white microscopic needles, slightly soluble in hot water, easily in alcohol, becoming discoloured at 300°, and melting at a higher temperature. The tetrabromobenzenesulphonic acid, of which the above are derivatives, possesses so great a similarity to that prepared by Beckurts, that they are considered to be identical. Beckurts gives the following structure to his tetrabromobenzenesulphonic acid:—



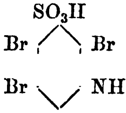
From this the acids prepared by the author would have the structure—



Tribromobenzenesulphonic acid.



Nitrotribromobenzenesulphonic acid.



Amidotribromobenzenesulphonic acid.

That the group NO_2 is carried to the meta-position on nitrating tribromobenzenesulphonic acid is proved by heating the amidodibromobenzenesulphonic acid, with hydriodic acid and amorphous phosphorus metamidobenzenesulphonic acid being thereby produced.

Amidodibromobenzenesulphonic Acid, $C_6H_2(NH_2)Br_2(SO_3H)$.—Mode of preparation already incidentally mentioned. Crystallises in small, white needles, which are anhydrous. Decomposes on heating without fusion. Soluble with difficulty in water and almost insoluble in alcohol. By heating with hydriodic acid and amorphous phosphorus in sealed tubes to 120°, it is converted into metamidobenzenesulphonic acid.

Potassium salt, $C_6H_2(NH_2)Br_2(SO_3K + 1{\cdot}5H_2O)$.—Microscopic needles in radiating groups. Easily soluble in water.

Barium salt, $[C_6H_2(NH_2)Br_2SO_3]_2Ba + 6H_2O$.—Long, white, or reddish needles, efflorescing in the air, and very soluble in water.

Calcium salt, $[C_6H_2(NH_2)Br_2SO_3]_2Ca + 2H_2O$.—Microscopic needles, very soluble in water.

Lead salt, $[C_6H_2(NH_2)Br_2SO_3]_2Pb$ (anhydrous).—Reddish, warty masses, consisting of small rhombic plates conglomerated. Easily soluble in water.

Diazo-compound.—Obtained in small quantities only by passing nitrous acid through water or alcohol in which the amidodibromobenzenesulphonic acid was suspended. When the acid was treated with concentrated hydrobromic acid, in which it remained suspended, and nitrous acid was passed through the liquid, heat being applied, the acid dissolved, with evolution of nitrogen, and the solution assumed a green colour. On evaporating on the water-bath, a residue remained, which, when recrystallised from hot water, yielded

Tribromobenzenesulphonic acid, $C_6H_2Br_3SO_3H$, crystallised in concentric groups of long needles.

Potassium salt, $C_6H_2Br_3SO_3K + 2H_2O$.—Shining, white, concentrically grouped needles, easily soluble in water.

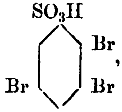
Barium salt, $[C_6H_2Br_3SO_3]_2Ba + 6H_2O$.—Precipitated from the solution of the acid on addition of barium chloride; purified by recrystallisation. Stellate groups of shining white needles.

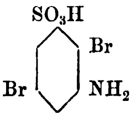
Calcium salt, $[C_6H_2Br_3SO_3]_2Ca + 5H_2O$.—Clusters of shining needles, easily soluble in water.

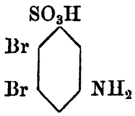
Lead salt, $[C_6H_2Br_3SO_3]_2Pb + 4H_2O$.—White needles, silky, easily soluble in water.

Sulphochloride, $C_6H_2Br_3SO_2Cl$.—Thick rhombic tables, melting at 85·5°.

Tribromobenzenesulphamide, $C_6H_2Br_3SO_2NH_2$. — Crystalline powder, consisting of microscopic plates. Blackens at 220—230°, and decomposes at higher temperatures.

With respect to the structure of the tribromobenzenesulphonic acid, the author considers that it is best represented by the following formula,  and that for the amidodibromobenzenesulphonic acid the two following structures are possible:—



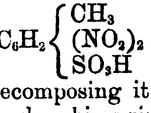


It is remarkable, however, that this latter acid is very similar to that which Berndsen and Beckurts obtained directly from metamidobenzenesulphonic acid and bromine. The differences are that these chemists found in the potassium salt, $1H_2O$, the author $1·5H_2O$. Beckurts found the solubility of his potassium salt as follows:—

100 grams of solution, after 48 hours at 10°, contained 3·10 grams of dry salt. The author found that 100 grams solution, after 48 hours at 20°, contained 7·069 grams of dry salt. The amidodibromobenzenesulphonic acid and the tribromobenzenesulphonic acid obtained therefrom by Reinke, and described by him, are very similar to those obtained by the author, so much so, that the author thinks it advisable to undertake a comparative investigation of these two compounds prepared by different methods. W. S.

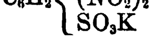
Dinitrotoluenesulphonic Acids. By H. SCHWANERT (*Deut. Chem. Ges. Ber.*, x, 29).—Engelhardt and Latschinoff have shown

(*Zeitschrift f. Chemie*, 1869, 617), that on treating toluene with sulphuric acid, two isomerides are formed, the para- and orthotoluenesulphonic acids. Engelhardt showed subsequently (*ibid.*, 1870, iv, 321) that by nitration of the paratoluenesulphonic acid, the same orthonitroparatoluenesulphonic acid was formed that Beilstein and Kuhlberg (*Liebig's Annalen*, clv, 8) obtained by dissolving orthonitrotoluene in sulphuric acid. By treating paranitrotoluene in the same manner, the latter obtained another sulpho-acid, formed also by nitration of a mixture of ortho- and paratoluenesulphonic acids, which therefore can be nothing but paranitroorthotoluenesulphonic acid. This was proved by Ascher (*Deut. Chem. Ges. Ber.*, iv, 650). Concerning dinitrotoluenesulphonic acids, the only notice is that of Beilstein and Kuhlberg (*Liebig's Annalen*, clv, 21), who found that by the action of nitric and sulphuric acids on toluene, they obtained a dinitrotoluenesulphonic acid, the lead salt of which they prepared. The author has undertaken the examination of the dinitrotoluenesulphonic acid, and finds that when a mixture of ortho- and paratoluenesulphonic acids, or of paranitroorthotoluenesulphonic and orthonitroparatoluenesulphonic acid is heated continuously with concentrated sulphuric acid, two dinitrotoluenesulphonic acids are obtained, one of which is formed (1) from the orthonitroparatoluenesulphonic acid; the other (2) from the paranitroorthotoluenesulphonic acid. To form the acid (1), orthonitroparatoluenesulphonic acid is boiled with concentrated sulphuric acid in a retort, for two or three days, the distillate being continually poured back again, till at last the acid comes over quite concentrated. The dinitro-acid is then produced. The resulting crystalline mass is dissolved out, the excess of sulphuric acid precipitated with lead carbonate, and the barium salt formed by addition of barium chloride. The resulting precipitate is pure barium dinitroparatoluenesulphonate. Paratoluenesulphonic acid may be treated in the same way with nitric acid, with equally good results. By treating a mixture of equal volumes of toluene and sulphuric acid with nitric acid of 1·5 sp. gr., slowly at first, then rapidly, and heating the mixture as described above, it is easy to separate the two isomeric barium salts, the barium dinitroparatoluenesulphonate crystallising out rapidly, and the barium dinitroorthotoluenesulphonate remaining in solution.



Dinitroparatoluenesulphonic acid, $C_6H_2\left\{\begin{array}{l}CH_3\\(NO_2)_2\\SO_3H\end{array}\right. + 2H_2O$.—The acid obtained from the barium salt by decomposing it with sulphuric acid, crystallises out in flat, pale-yellow, rhombic prisms, changing on the filter to a yellow powder. They change to sulphur-yellow in sunshine, absorb water slowly, and are easily soluble in water, alcohol, and ether; they soften at 110°, give off their water at 140°, and melt at 165°.

The salts of the dinitroparatoluenesulphonic acid are for the most part difficultly soluble in water, change colour on exposure to light, and explode on being strongly heated.



Potassium salt, $C_6H_2\left\{\begin{array}{l}CH_3\\(NO_2)_2\\SO_3K\end{array}\right.$.—Obtained by decomposing the barium salt with potassium carbonate; crystallises from water in long, white rhombic prisms; from alcohol in small, shining, highly refractive plates. Light changes it to a brown red.

Ammonium salt, $C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\SO_3NH_4\end{matrix}\right.$.—Formed by treating the acid with ammonia; white, flat rhombic prisms, easily bent.

Barium salt, $\left[C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\SO_3\end{matrix}\right.\right]_2Ba + 4H_2O$.—White, silky, pliable, very bitter prisms, which do not lose their water completely below 160°.

Calcium salt, $\left[C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\SO_3\end{matrix}\right.\right]_2Ca + 2H_2O$.—Groups of white needles, or scales.

Lead salt, $\left[C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\SO_3\end{matrix}\right.\right]_2Pb + 2H_2O + 3H_2O$.—Obtained by decomposing the barium salt with sulphuric acid, and neutralising with lead carbonate. From the hot aqueous solution it crystallises in yellowish, warty clumps of needles, containing 2 mols. water; from the concentrated mother-liquor, in yellow laminæ with 3 mols. water.

Copper salt, $\left[C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\SO_3\end{matrix}\right.\right]_2Cu + 4H_2O$.—Blue-green oblique rhombic prisms.

Dinitroparatoluenesulphonic chloride? $C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\SO_2Cl\end{matrix}\right.$.—Prepared by the continuous heating of 1 part potassium salt and 2 parts phosphorus chloride, at 150°. White, rhombic needles, soluble in ether and alcohol, melting at 125°.

Dinitroparatoluenesulphamide? $C_6H_2\left\{\begin{matrix}CH_3\\(NO_2)_2\\(SO_2NH_2\end{matrix}\right.$.—Prepared from the chloride by treatment with strong ammonia; crystallises from water in laminæ similar to benzoic acid; from alcohol in white needles melting at 203°. An amidonitroparatoluenesulphonic acid cannot be prepared by treating dinitroparatoluenesulphonic acid with ammonium sulphide; even though the greatest care may be taken to prevent rise of temperature, the formation of the following compound invariably takes place:—

Diamidoparatoluenesulphonic acid, $C_6H_2\left\{\begin{matrix}CH_3\\(NH_2)_2\\SO_3H\end{matrix}\right.$.—Crystallises from water in shining, rhombic needles, becoming grey by the action of light; melting point above 280°. With bases no well defined salts are formed, but with acids it yields highly crystalline compounds, losing their water at 120—140°, crystallising unchanged from acids, but losing part of the acid when crystallising from water.

The *hydrochloride* and *hydrobromide*, $C_6H_2\left\{\begin{matrix}CH_3\\(NH_2)_2\\SO_3H\end{matrix}\right.\left\{\begin{matrix}HCl\\\text{or }HBr\end{matrix}\right\} + 2H_2O$, form large, white crystals, soluble in water.

The *nitrate*, $C_6H_2\left\{\begin{matrix}CH_3\\(NH)_2.HNO_3\\SO_3H\end{matrix}\right. + H_2O$, forms small, reddish needles.

Sulphate, $\left[C_6H_2\left\{\begin{matrix}CH_3\\(NH_2)_2\\SO_3H\end{matrix}\right.\right].2H_2SO_4 + 4H_2O$.—Transparent, white scales. On cautiously treating this salt in the cold with nitrous acid and absolute alcohol, the diazo-compound is formed as a brown powder, which when dry explodes below 100°.

Bromodiamidoparatoluenesulphonic acid, $C_6H\left\{\begin{matrix}CH_3\\(NH_2)Br\\SO_3H\end{matrix}\right.$.—Formed by treating the diamidoparatoluenesulphonic acid with hot water and bromine, added drop by drop. The pure diamidodibrominated acid is never formed, even on addition of a great excess of bromine, but ammonium bromide is nearly always produced.

Bromodiamidoparatoluenesulphonic acid forms small, shining, greyish-green crystals; also short, oblique rhombic plates, difficulty soluble in water. It unites with bases, but not with acids.

Potassium salt, $C_6H\left\{\begin{matrix}CH_3\\(NH_2)_2\\Br\\SO_3K\end{matrix}\right. + 2\frac{1}{2}H_2O$.—Formed by the action of potassium carbonate on the hot aqueous solution of bromodiamidoparatoluenesulphonic acid. Crystallises out over oil of vitriol, in flat, yellow needles, easily soluble in water. Loses water, but not colour, at 100°. Heated to 120°, it turns blue, dissolving in water, with a fine blue colour. The *barium salt*, produced under the same conditions, forms small grey crystals and behaves in a similar manner. On adding 1 mol. bromine to 1 mol. diamidoparatoluenesulphonic acid, a grey-green precipitate is formed, and much ammonium bromide remains dissolved. On heating the powder with hydrobromic acid and amorphous phosphorus under pressure, at 120°, the bromine is removed, and diamidoparatoluenesulphonic acid reproduced.

The authors are engaged on experiments to show the structure of the above compound. C. L. F.

Mutual Solubility of Phenol and Water. By W. ALEXEJEFF (*Deut. Chem. Ges. Ber.*, x, 410—412).—It was found that only those solutions accord with the hypothesis of Dossios, and increase in solubility with the temperature, which either form no hydrates, or stable ones. Thus he has discovered that there is an increase of solubility in the case of phenol (whose hydrate is stable) and water, with the increase of temperature. He has also shown that in the case of amyl-alcohol (which forms a very unstable hydrate) and water, the solu-

Amount of phenol in 100 parts aqueous solution	3·75	4·83	4·85	5·13	5·27	13·78	17·3	17·97	18·78	20·05	
Temperature at which the solution becomes just clear	Not turbid at – 10°	+ 11°	+ 12°	+ 25°	+ 26°	+ 80°	+ 82°	+ 83°	+ 83°	+ 83°	
Amount of phenol in 100 parts of solution...............	5·36	6·19	7·33	8·03	9·83	11·83	23·77	24·12	33·23	37·39	40·01
Temperature.................	+ 35°	+ 45°	+ 58°	+ 59°	+ 72°	+ 77°	+ 84°	+ 84°	+ 84°	+ 84°	+ 84°
Amount of water in 100 parts of solution...............	16·38	19·85	20·92	23·3	26·75	26·93	31·99	34·44			
Temperature...............	Not turbid at – 10°	..	– 5°	+ 9°	+ 32°	+ 43°	+ 53°	+ 60°			
Amount of water in 100 parts of solution...............	34·77	35·10	40·72	47·54	49·52	59·85	59·99	66·77	76·23		
Temperature.................	+ 61°	+ 62°	+ 71°	+ 78°	+ 80°	+ 84°	+ 84°	+ 84°	+ 84°		
Amount of amyl alcohol in 100 parts of water	4·23	3·89	3·50	2·99	2·72	2·50	2·34	2·34	2·50	2·72	
Temperature.................	0°	+ 4°	+ 8°	+ 18°	+ 24°	+ 31°	+ 49°	+ 57°	+ 81°	+ 90°	
Amount of water in 100 parts amyl alcohol.............	8·92	9·29	9·73	10·21	19·74	10·98	12·48	12·58	13·65	14·33	14·98
Temperature.................	+ 8°	+ 19°	+ 26°	+ 34°	+ 44°	+ 45°	+ 66°	+ 68°	+ 79°	+ 84°	+ 90°

bility of the former in the latter decreases with increase of temperature. This phenomenon is similar to that observed in the case of Glauber's salt, and may be accounted for probably in the same way, viz., by assuming that the hydrate suffers decomposition at that particular temperature.

The estimations of miscibility were made as follows:—Scaled glass tubes, containing weighed quantities of phenol and water, or amyl alcohol and water, were warmed in a beaker filled with water, till their contents became clear. The heating was then discontinued, and cold water was gradually added, with constant stirring, till turbidity just commenced to set in, when the temperature was at once observed. Thus the temperature was determined, at which the weighed quantities of the solutions are just miscible. (See Table, p. 473.)

W. S.

α-Amidonitrophenol. By K. STUCKENBERG (*Deut. Chem. Ges. Ber.*, x, 382—385).—This compound yields readily monobenzoyl-amidonitrophenol, the reaction beginning in the cold; it crystallises from aniline in small, yellow needles. On dissolving it in a cooled mixture of nitric and glacial acetic acids, it yields benzoyl-amidodinitrophenol, crystallising in small, pale green prisms melting at 218—219°. On heating it with hydrochloric acid to 130°, amidodinitrophenol is obtained, crystallising from alcohol in dark red needles, and from chloroform in glistening, monoclinic prisms, melting at 169—170°. This compound appears to be identical with picramic acid. C. S.

Resorcin. By L. CALDERON (*Compt. rend.*, lxxxiv, 779—782). —The fusing point of the crystals is placed by the author at 118°, or 18° above that usually stated (100°). The vapour-density he determines to be 3·807. The molecular volume is very nearly the same as that of benzene. Resorcin dissolves in water, producing a sensible lowering of temperature. 100 grams of water at 0° dissolve about 86·4 grams of resorcin. R. R.

Methyl Ethers of Resorcin. By J. HABERMANN (*Deut. Chem. Ges. Ber.*, x, 867—870).—The two methyl ethers of resorcin are easily prepared by heating an intimate mixture of 1 molecule of resorcin, 2 molecules of potassium methyl-sulphate, and 2 molecules of potash, with a little absolute alcohol, for 4—5 hours, to 160°. The product is acidulated with sulphuric acid, and exhausted with ether. After the latter has been driven off, the residue is distilled with water, the dimethyl ether passing over, while resorcin and the monomethyl ether remain behind, which are extracted by ether, and separated by fractional distillation.

Monomethylresorcin, $C_6H_4\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$, is a colourless or pale yellow, very refractive liquid, which is tolerably soluble in cold, more freely in hot water and dilute alcohol, and mixes in almost every proportion with absolute alcohol and ether. It has only a faint odour, but its dilute alcoholic solution has an aromatic, but not agreeable smell. Its aqueous solution tastes sweetish and burning, and is coloured violet by ferric chloride. Methylresorcin boils at 243—244°, and becomes at

— 17·5° viscid, but not crystalline. With alcoholic potash it forms a thick, syrupy mass, which turns reddish-brown in the air.

Dimethylresorcin, $C_6H_4(OCH_3)_2$, is a heavy, colourless oil, boiling at 214—215°, dissolves but sparingly in cold, more freely in boiling water and dilute alcohol, and in every proportion in absolute alcohol and ether. Its aqueous solution is not coloured by ferric salts.

C. S.

Conversion of Metanitrophenol into Trinitroresorcin. By A. BANTLIN (*Deut. Chem. Ges. Ber.*, x, 524).—The well crystallised compound, which is obtained by treating metanitrophenol or the two isomeric dinitrophenols with concentrated nitric acid, is not, as formerly stated, trinitrophenol, but *trinitroresorcin* (styphnic acid). The hydroxyl group enters into the molecule simultaneously with the third nitro-group. Griess has found (see this Journal, xiii, 263), and Salkowski has confirmed the fact, that styphnic acid is formed also by the action of nitric acid on orthonitrobenzoic acid. G. T. A.

β-Diamidophenol and Derivatives. By K. STUCKENBERG (*Deut. Chem. Ges. Ber.*, x, 385—388).—This diamidophenol was obtained by reducing diorthonitrophenol. The hydrochloride, $C_6H_3OH(NH_2)_2(HCl)_2$, was purified like the α-compound; it crystallises from hot dilute hydrochloric acid in thick needles. $C_6H_3OH(NH_2)_2SO_4H_2$ is sparingly soluble in alcohol, freely in water, and crystallises in small glistening needles. On heating the diamidophenol with benzoyl chloride, the compound, $C_6H_3OH(NH.CO.C_6H_5)_2$, is formed, crystallising from benzene in small short prisms melting at 209—213°. At the same time the tribenzoyl and tetrabenzoyl-compounds are formed. The former is insoluble in chloroform, and crystallises from alcohol in needles melting at 183—184°, while the latter deliquesces in chloroform, and forms thin plates melting at 182°.

β-Amidonitrophenol was obtained by reducing β-dinitrophenol with ammonium sulphide; it forms red needles melting at 110—111°, and dissolves readily in most solvents, but sparingly in cold water. It is much more stable than the α-compound.

$C_6H_3(NO_2)(OH)NH_2.SO_4H_2$ crystallises in microscopic prisms.

C. S.

Paradiamidotoluene and Toluquinone. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 832—835).—By the action of tin and hydrochloric acid on orthamido-azotoluene, it is resolved into orthotoluidine and paradiamidotoluene, $C_7H_6(NH_2)_2$. The latter crystallises from hot benzene in plates, which are grouped in rosettes, and melt at 64° to a colourless oil, boiling at about 280°. It is freely soluble in water, alcohol, and ether; its aqueous solution becomes red in the air, and deposits a brown amorphous body. The hydrochloride, $C_7H_6(NH_2.ClH)_2$ is readily soluble in water, sparingly in concentrated hydrochloric acid, and crystallises in small pearly plates. On adding to its solution oxidising agents, such as ferric chloride, potassium dichromate, manganese dioxide, platinic chloride, &c., it assumes a beautiful green colour, which soon changes to a dirty red, *toluquinone* being formed, which is conveniently prepared by distilling the base with dilute sulphuric acid and manganese dioxide. It forms golden yellow plates, smelling like common quinone, dissolves sparingly in cold, more readily in hot water, and freely in alcohol and ether. Its aqueous solution is coloured deep brownish-red by alkalis. Reducing agents convert it into *toluhydroquinone*, crystallising from benzene in broad, colourless needles, melting at 124°. It dissolves very freely in water, alcohol, and ether, and more sparingly in benzene. On mixing aqueous solutions containing equal numbers of molecules of the quinone and hydroquinone, a yellowish-brown liquid is formed, containing the *quinhydrone*, which is isolated by exhausting the solution with ether and evaporating. It crystallises in almost black needles, which have a yellowish metallic lustre, and show in transmitted light a violet colour. They melt at 52°, and dissolve in water with a yellowish-brown, and in ether with a yellow colour. C. S.

Nitrotoluquinone and Chloranilic Acid. By A. ETARD (*Compt. rend.*, lxxxiv, 614—617).—Nitrotoluquinone is formed by the action of chlorochromic acid on nitrotoluene. The reaction is effected in a globe containing the nitrotoluene heated to 200°, to which the acid is added in small quantities, 4—5 grms. at a time. The product treated with water deposits nitrotoluene, and the liquid contains nitrotoluquinone and chromium chloride. The chromium having been got rid of by excess of soda, the filtrate is boiled with animal charcoal and afterwards slightly acidified. The nitrotoluquinone separates nearly pure. The precipitate having been washed on a filter with a little cold water, a saturated solution of it is made in boiling water, from which it is finally deposited in large brown lamellar crystals. These melt at 237° and then sublime.

Chloranilic acid was obtained by treating paradibromobenzene with chlorochromic acid as above. F. J. L.

Constitution of Oxythymoquinone. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 611—614).—The dinitrothymol which is formed by nitrating nitrosothymol is identical with that from thymolsulphonic acid. The following salts were prepared and analysed.

$C_{10}H_{11}(NO_2)_2OK$ forms long yellow anhydrous needles.

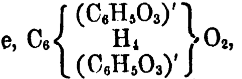
$[C_{10}H_{11}(NO_2)_2O]_2Ba + 3H_2O$ crystallises from boiling water in orange needles, which on drying at 145° become dark red.

$[C_{10}H_{11}(NO_2)_2O]_2Ca + 5H_2O$ is readily soluble in dilute alcohol, and forms orange needles, which at 145° turn red, and in moist air again orange. In one experiment a lemon-yellow salt.

$[C_{10}H_{11}(NO_2)_2O]_2Ca + 7H_2O$ was obtained.

$C_{10}H_{11}(NO_2)_2OAg$ is a yellow precipitate crystallising from alcohol in pale yellow needles.

The identity of the two dinitrothymols is further proved by the fact that on oxidising nitrosothymol, the same mononitrothymol is obtained which is formed as first product of the action of nitric acid on thymolsulphonic acid. It is easily prepared by heating an aqueous solution of the acid with nitric acid not above 50° until a yellowish-white precipitate is formed. It is washed, dried, treated with cold petroleum-naphtha, and then crystallised from the same liquid. It forms very thin, colourless needles with a bluish fluorescence, melting at 140°; its ammonium and potassium salts are very soluble. As this compound is present in crude dinitrothymol, the oxythymoquinone obtained from the latter contains some thymoquinone, which lowers its melting point. This, however, is not the cause of the varying melting point of pure oxythymoquinone, which sometimes is as high as 187°, sometimes as low as 169°. The reason is perhaps that the compound undergoes a molecular change like thymoquinone, which when kept in the moist state becomes covered with a white opaque layer. On washing with ether or distilling with steam, this body remains behind; it crystallises from alcohol in yellow-white needles melting at 200°, and seems to be a polymeride. C. S.

Contribution to the Knowledge of Pyrogallol. By OSCAR LOEW (*J. pr. Chem.* [2], xv, 322—327).—An aqueous solution of pure pyrogallol oxidises too slowly for the observation of its oxidation-products in a short time, whereas in presence of alkalis or alkaline carbonates, the process is too rapid. A solution of pyrogallol and sodium phosphate is found to give the best results, and to produce, on exposure to the air for 1—2 weeks, three different substances, namely (*a*) acicular crystals which can be separated from the solution by ether; (*b*) a crystalline body separated from the solution by means of ether, after addition of hydrochloric acid; and (*c*) an insoluble precipitate formed on acidifying: by oxidation in this manner carbonic anhydride is produced, but not oxalic or acetic acid. Solutions of pyrogallol and other salts were also observed, and it was found that the acetates, borates, &c., of the alkalis have the same effect on pyrogallol, but in a less marked degree. A remarkable exception is found in the case of sodium thiosulphate, which, without being itself oxidised, exerts a powerful oxidising effect. Sodium and potassium chlorides, nitrates, and sulphates produce no accelerating effects, which are obtained to a small extent by ammonium and magnesium sulphates, and potassium iodide. The author has constructed a piece of apparatus in which the mixtures can be thoroughly shaken together with oxygen, whereby a saving of time is effected. He finds, however, that at a temperature of 50°, the machine being kept in action for half an hour (*a*) these are formed in small quantity only, whereas (*b*) and (*c*) predominate, whereas at a temperature of 16° rising towards the end to 25°, and with half the quantity of phosphate, the quantity of (*a*) increases, amounting to 10 per cent. of the pyrogallol employed. The acicular crystals (*a*) above referred to, are almost insoluble in pure water, and are decomposed by alkalis or alkaline carbonates with deep blue coloration; they are red when deposited from ether, and can be sublimed, melting at a temperature above 200°. The aqueous solution is precipitated brown by ferrous sulphate, reddish-brown by copper and lead salts. The analyses show that the compound is pyrogallo-quinone,  $C_6\left\{\begin{matrix}(C_6H_5O_3)'\\H_4\\(C_6H_5O_3)'\end{matrix}\right\}O_2$, in which more than one hydrogen is replaceable by a metal, thus $C_{18}H_{10}Pb_2O_8$ and $C_{18}H_{12}PbO_8$. It appears that this substance is a most delicate test for oxygen, for in presence of sodium carbonate, a dark yellow coloration is produced with the slightest trace of oxygen.

In concentrated solution, pyrogallol absorbs nitric oxide and cyanogen, forming a crystalline precipitate of pyrogallol cyanide, ($C_6H_6O_3.CN$). This substance gradually decomposes by keeping, or rapidly on heating to 100°, into white needles (pyrogallol ?), and a brownish-red resinous body soluble in alcohol. Hydrochloric acid decomposes it into a crystalline body, which when heated gives off carbonic anhydride. Pyrogallol likewise combines with cyanamide.

E. W. P.

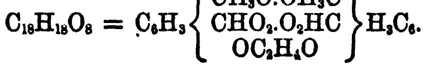
Researches on the Substituted Eugenols. By A. CAHOURS (*Compt. rend.*, lxxxiv, 1195—1201).—When methylpropylprotocatechuic acid (*Chem. Soc. J.*, 1877, i, 460) is warmed with nitric acid of sp. gr. 1·36, it dissolves, with evolution of nitrogen oxide, and if, when the action has ceased, water be added, a yellow crystalline substance separates, which is insoluble in cold, slightly soluble in hot water, and only partially soluble in ammonia or dilute potash.

The portion insoluble in alkali, when crystallised from hot alcohol, separates in sulphur-yellow, leaf-like crystals, and is probably a nitro-derivative of *methylpropylpyrocatechin.* Treated with tin and hydrochloric acid, it dissolves gradually, and separates on evaporation in needle-shaped crystals. These, when treated with potash, give a precipitate of oxide of tin, mixed with a substance which is coloured brown in contact with the air, and dissolves in hydrochloric acid, forming a red solution, from which ammonia throws down a brown precipitate.

The portion dissolved in ammonia is thrown down by hydrochloric acid in the form of yellow flakes, soluble in boiling water, from which it separates on cooling, in small, shining, yellow prisms. It is probably *mononitromethylpropylprotocatechuic acid*, as it gives by analysis, 51·3 p. c. for carbon, and 5·4 hydrogen, the formula, $C_{11}H_{13}NO_6$, requiring 51·8 C., 5·1 H., 5·5 N., and 37·6 O.

Methylpropylprotocatechuic acid, when distilled with sand and powdered baryta, gives an aromatic oil, boiling at 240—245°, and giving, on analysis, numbers approximating to those required for *methylpropylprotocatechin.*

Ethene-eugenol, formed by the action of ethene dibromide on potassium eugenol, is attacked by potassium permanganate in the same way as the methyl- and ethyl-eugenols. The acid, liberated from its potassium salt by hydrochloric acid, is nearly insoluble in cold water, slightly soluble in hot water and in alcohol, more so in ether, from which it separates as an amorphous, yellow mass. Analysis gave the following numbers: $C = 60·0$; $H = 5·4$, which lead to the formula of *ethene-dimethylprotocatechuic acid*, $C_{18}H_{18}O_8$, the formation of which is easily explained by supposing that two groups, C_3H_5, in the molecule of ethylene-eugenol, are replaced by two carboxyl-groups—



$$C_{18}H_{18}O_8 = C_6H_3\left\{\begin{matrix} CH_3O.OH_3C \\ CHO_2.O_2HC \\ OC_2H_4O \end{matrix}\right\}H_3C_6.$$

Nitric acid of sp. gr. 1·48 attacks it, on heating, with disengagement of red vapours, and the liquid on cooling deposits transparent, yellow crystals. Distilled with sand and baryta, it forms a yellow, aromatic oil.

Phosphorus pentachloride acts violently on ethene-eugenol, when gently heated. Large quantities of hydrochloric acid are evolved, and the liquid in the receiver consists of trichloride and oxychloride of phosphorus. The residue in the retort, after washing with water, consists of a brownish-yellow resin, insoluble in water, slightly soluble in alcohol and ether, from which it is deposited as an amorphous mass. It appears to be a substitution-derivative of ethene-eugenol. Trimethene iodide, when heated in sealed tubes with potassium-eugenol, either in the water-bath or to 150° in an oil-bath, gives rise only to resinous bodies, which have not been studied.

Trimethene dibromide (50 grams) heated for some hours in a water-bath in sealed tubes, with an equivalent proportion of potassium eugenol in presence of alcohol, gave an abundant deposit of potassium bromide. On cooling, the liquid became filled with magnificent crystals, of a substance which, when washed with potash and water, dried between blotting-paper, and dissolved in boiling alcohol, separated out in nearly colourless crystals, and, after recrystallisation from ether, formed colourless, satiny crystals closely resembling ethene-eugenol. From alcohol it separates out as small, shining, colourless prisms. Analysis gave 74·82 and 74·93 p. c. carbon, 7·71 and 7·81 hydrogen, agreeing nearly with the formula of *propene-eugenol*, $C_{23}H_{28}O_5$, or $C_{20}H_{22}(C_3H_6)O_4$, which requires 75·0 p. c. C., 7·6 H., and 17·4 O.

The constitutional formula of this body is—

$$C_{23}H_{28}O_4 = C_6H_3\left\{\begin{array}{l} CH_3O.OH_3C \\ C_3H_5.H_5C_3 \\ O{-}C_3H_6{-}O \end{array}\right\}H_3C_6.$$

Potassium permanganate acts on it in the same way as on its lower homologues. Hydrochloric acid precipitates a yellowish, flocculent, non-crystalline substance, scarcely soluble in boiling water, which is *propene-dimethylprotocatechuic acid.* Analysis gives C = 61·05; H = 5·62. The formula $C_{19}H_{20}O_8$, requires C = 60·64; H = 5·32.

The action of the two bodies isomeric with trimethene dibromide, viz., methylbromacetol and propene bromide, on potassium-eugenol, is somewhat different.

The latter body was heated in sealed tubes with potassium-eugenol and alcohol. The alcoholic liquid separated from the potassium bromide was evaporated, and the residue washed with potash and water; it then formed a heavy, aromatic oil, which deposited a few crystals of a compound which, when pressed between blotting-paper, and recrystallised from ether, formed needle-shaped crystals melting at 56—58°. Analysis gave numbers leading to the formula, $C_{23}H_{28}O_4$. The body is therefore an isomeride of propene-eugenol.

C. W. W.

Constitution of the Radicle, C_3H_5, in Eugenol and Anethol.

By E. ERLENMEYER (*Deut. Chem. Ges. Ber.*, x, 628—634).—As these compounds yield acetic acid on oxidation it would appear that they contain the group methylvinyl, $CH_3—CH{=}CH—$. But this becomes doubtful, since the author has found that salicylic acid and metaoxybenzoic acid also yield acetic acid, whereas methyleugenol yields only a very small quantity. It appears, therefore, more probable that eugenol contains the radicle allyl, $CH_2{=}CH—CH_2—$; anethol, however, which readily yields anisic and acetic aldehydes and their acids, seems to contain methylvinyl.

Tiemann and Haarmann obtained from coniferin the compound, $C_9H_{12}O_3$, which they first regarded as ethylvanillin, $C_6H_3\left\{\begin{array}{l}OCH_3\\OC_2H_5\\COH\end{array}\right.$, since on heating it with hydriodic acid it yielded methyl iodide, ethyl iodide, and protocatechuic acid; but they have since shown that it is $C_6H_3\left\{\begin{array}{l}OCH_3\\COH\\C_3H_4.OH\end{array}\right.$, which formula does not explain the formation of the two latter products. C. S.

Constituents of Corallin. By KARL ZULKOWSKI (*Deut. Chem. Ges. Ber.*, x, 460—463).—The author finds that the colouring matter prepared by Kolbe and Schmitt's process, and known in commerce as corallin, is not a definite chemical compound, but a mixture of two substances, in about equal proportions.

When corallin is dissolved in soda and treated with sulphur dioxide, there is thrown down a large quantity of a resinous body, which melts in boiling water, and solidifies to a hard, brittle, pale-red mass, devoid of metallic lustre. This substance, which the author calls provisionally *pseudorosolic acid*, is oxidised in alkaline solution by potassium ferricyanide and other oxidising agents, and thus yields a dark-red body, soluble in alkalis with violet-red colour, and in alcohol.

The other constituent of corallin is rosolic acid. J. R.

Metanethol Camphor. By P. PERRENOUD (*Liebig's Annalen*, clxxxvii, 63—79).—The exact relationship between the four isomeric bodies, anethol, metanethol, anisoïn, and metanethol camphor, is a question still of much uncertainty. With a view to throwing additional light on the subject, the author has determined to study metanethol camphor. Metanethol camphor was prepared by heating fused anethol, with three and a half times its weight of powdered zinc chloride, and distilling in a current of steam. Metanethol camphor forms, when pure, long glittering needles, melting at 132°, and boiling above 300°, whilst partially subliming at a lower temperature. It is very easily soluble in boiling acetic acid, not so easily soluble in hot ether and alcohol, readily soluble in chloroform, carbon bisulphide, benzene, and concentrated sulphuric acid, slightly soluble in cold ether and alcohol. It is insoluble in water and sodium hydrate solution. It is readily acted on by nitric acid, and forms substitution-compounds with bromine. These are being further examined. On analysis metanethol camphor yields numbers closely agreeing with the formula, $C_{10}H_{12}O$.

The view taken by Gerhardt that anethol and metanethol camphor are isomeric, is therefore fully confirmed.

With concentrated sulphuric acid, metanethol camphor forms a sulpho-acid, $C_{10}H_{11}(SO_3)O.H$. The calcium salt forms large plates, containing 1 molecule of water, readily soluble in water and alcohol. The barium salt crystallises in long, glittering needles, uniting in groups, and containing 1 molecule of water of crystallisation. They are slightly soluble in absolute alcohol, more soluble in dilute alcohol, and readily soluble in water. The sodium salt forms needle-like crystals. By acting with phosphorus pentachloride on sodium metanetholcamphorsulphate, a chlorinated body of the formula, $C_{10}H_{11}O_1SO_2Cl$ is obtained. It forms fine crystals, melting at 182—183°, and readily soluble in ether, chloroform, and acetic acid. E. N.

On Salicylol. By T. L. Phipson (*Chem. News*, xxxv, 225).—An attempt was recently made by the author to obtain the essence of *Spiraea ulmaria*, by oxidising a mixture of phenol and grape-sugar, with the aid of potassium bichromate and sulphuric acid. A large amount of resinous substances was produced, but on following up the action of the bichromate by permanganate of potassium, a moment arrives when the odour of phenol ceases, and a strong odour of the plant arises. This occurs at 50°, but the addition of more permanganate causes it to vanish. A minute quantity of salicylol was, however, obtained on distillation.

In preparing nitro-salicylic acid by heating to boiling artificial salicylic acid with diluted fuming nitric acid, the solution becomes dark reddish-brown, and emits at the same time a strong odour of salicylol. In heating salicylic acid mixed with water with nitrite of potassium, a still larger quantity of salicylol is produced. By adding a little sulphuric acid to the liquid, whilst still warm, the nitrosalicylic acid separates in fine needles on cooling. D. B.

Chlorinated Acetophenone. By R. Dyckerhoff (*Deut. Chem. Ges. Ber.*, x, 531—533).—During the preparation of the chloride $C_6H_5COCH_2Cl$, more chlorine was passed into the vapour of the boiling acetophenone than sufficed for taking up one atom. The product obtained was essentially different from the ordinary one. On fractional distillation a liquid passed over at 250—255°, which consisted chiefly of the bichloride $C_8H_6OCl_2$.

By continued action of chlorine, a dark thick mass was obtained, which, on distillation, yielded a small quantity of a liquid consisting chiefly of benzoyl chloride. The part with highest boiling point contained products poorer in chlorine. Analyses gave numbers pointing to the formula $C_{16}H_{11}O_2Cl$. Possibly this body was formed in a similar way to the chlorides obtained by Staedel (*Berichte*, ix) by removal of hydrochloric acid from two molecules of $C_6H_5COCH_2Cl$. At a temperature above 360° a substance passed over which solidified in amorphous masses on cooling, and emitted a smell of oil of bitter almonds. The occurrence of benzoic acid was also noticed. The formation of benzoyl chloride and benzoic acid may be explained in two ways:—

1. It may be supposed that chlorine was gradually substituted for

the hydrogen-atoms of the methyl-group, and finally split off, the CCl_3 residue taking its place, and forming benzoyl chloride. Tetrachloride of carbon must have been formed at the same time, though it could not be detected—possibly it was carried off by the stream of chlorine. In the preparation of $C_6H_5COCH_2Cl$ water is always formed, which may possibly convert the benzoyl chloride partly into benzoic acid.

2 The water formed out of the acetophenone may, in presence of the chlorine, exercise an oxidising influence, so that from a small part of the acetophenone, benzaldehyde may be first formed, which may then be partly converted, by further oxidation, into benzoic acid, while another part passes, under the influence of the chlorine, into benzoyl chloride.

The formula and constitution of the body $C_6H_5CCl{=}CHCl$ (called α-β-bichlorostyrol in a former paper), which is obtained by the action of phosphorus pentachloride on acetophenone with a chlorinated methyl-group, is confirmed by further experiments. It consists of a colourless, oily liquid, boiling at 221° (uncorrected), and possessing a pleasant odour. On passing chlorine into the cold liquid, a body is obtained which seems to be phenylised perchlorethylene. The following formulæ show its mode of origin:—

$$C_6H_5CCl{=}CHCl + Cl_2 = C_6H_5CCl_2{-}CHCl_2$$
$$C_6H_5CCl_2{-}CHCl_2 = C_6H_5CCl{=}CCl_2 + HCl.$$

In odour this liquid resembles benzoyl chloride.

With bromine a substance is obtained which crystallises in bright transparent laminæ, and volatilises at ordinary temperatures with separation of a halogen hydride.

An attempt to separate hydrochloric acid by boiling with an alcoholic solution of potassium cyanide was unsuccessful, which shows that the chlorine is firmly united to the carbon-atom next to the benzene nucleus. The action of an alcoholic solution of an alkali has not been accurately determined, but it seems as if the chlorine-atom which occupies the α-position $(C_6H_5\underset{\beta}{C}Cl{=}\underset{\alpha}{C}HCl)$ is in some way exchanged.

G. T. A.

On two Isomeric Bromonitrophenylacetic Acids. By P. P. BEDSON (*Deut. Chem. Ges. Ber.*, x, 530—531).—By nitration of parabromophenylacetic acid two nitro-products are obtained. When these are dissolved in a hot mixture of two volumes of alcohol to one of water, an acid which melts at 167—169° separates out on cooling. If the mother-liquor is concentrated, and the acids are converted into their barium salts, one of them, which is soluble with difficulty, yields an acid melting at 112—115°, the other and more easily soluble one gives an acid which melts at 167—169°. The first of these acids is easily soluble in hot water, and crystallises from the solution in flattened, faintly greenish-yellow needles, with nacreous lustre. On oxidation with bichromate it is converted into a bromonitrobenzoic acid, melting at 197—199°, and agreeing in properties with the body prepared by Stübner (*Ann. Chem. Pharm.*, clxiii, 248) from parabromobenzoic acid, in which the nitro-group takes the meta-position. It is therefore parabromometanitrophenylacetic acid.

The acid which forms the easily soluble barium salt dissolves with difficulty in hot water, and crystallises in almost colourless ramifying needles, which melt at 167—169°. The nitro-group in this body must occupy the ortho-position. G. T. A.

Synthesis of Nitro-acids. By F. Fittica (*Deut. Chem. Ges. Ber.*, x, 489).—When ethyl nitrate is dropped into a solution of cinnamic acid in sulphuric acid, ortho- and paranitrobenzoic acids are formed.

Ethyl nitrate added to a solution of benzaldehyde in concentrated sulphuric acid produces a substance which yields, by oxidation with chromic acid, a nitrobenzoic acid melting at 135°. J. R.

Nitrobenzoic Acids. By F. Fittica (*Deut. Chem. Ges. Ber.*, x, 481—486).—The author has obtained, by the action of ethyl nitrate on an ethereal solution of benzoic acid, in presence of strong sulphuric acid, a nitrobenzoic acid, $C_6H_4(NO_2)COOH$, which melts at 127°, and dissolves in 380 parts of water at 16°.

The silver salt of this acid, when digested with ethyl iodide at temperatures not exceeding 18°, yields an ether which crystallises in small yellowish needles melting at 37°, and dissolving easily in alcohol and ether, but not in water. The salts of the foregoing nitrobenzoic acid are readily converted by recrystallisation into salts of the isomeric metanitrobenzoic acid. The free acid, however, is not thus transformed, either by recrystallisation or by heating above its melting point.

The author described in a previous paper another acid isomeric with the above, melting at 135°. This acid, he now finds, yields an ether identical with that obtained from the acid melting at 127°.

Besides the two acids mentioned above, the author has obtained two other acids of the same composition, melting at 128° and 142°, and differing in physical characters from those previously described. They are lemon-yellow, crystalline bodies, dissolving more freely in water than the other acids, and forming lemon-yellow barium, silver, and lead salts, which again yield yellow acids by decomposition. Their ethers are also yellow.

a. The acid melting at 128° was obtained by dropping a mixture of benzoyl chloride and ethyl nitrate in molecular proportions into concentrated sulphuric acid at 70° to 80°. It crystallises in needles which dissolve in 284·5 parts of water at 16°.

b. The acid melting at 142° was obtained by dissolving benzoic acid (1 mol.) in concentrated sulphuric acid, and dropping ethyl nitrate (1 mol.) into the solution. It closely resembles the acid *a*, but requires for solution 309 parts of water at 16°. J. R.

Benzonitrobenzoic Acid. By F. Fittica (*Deut. Chem. Ges. Ber.*, x, 486—488).—The ethyl-compound of an acid thus named by the author is formed, together with other products, when a mixture of benzoic acid in ethereal solution with an equal number of molecules of ethyl nitrate is dropped into concentrated sulphuric acid, and the whole is kept at 50° for some time. It is isolated from the crude product by fractional distillation, and boils at 282—285°. Analysis shows it to have the composition of a molecular combination of ethyl benzoate with ethyl nitrobenzoate:—

$$C_6H_5COOC_2H_5.C_6H_4(NO_2)COOC_2H_5,$$

and its chemical behaviour agrees with this view. The ether is a greenish liquid of faint, somewhat pungent odour. It distils almost without decomposition. When saponified with potash it yields an acid melting at 137°, which, from its behaviour with sodium carbonate, the author regards as a combination of benzoic acid with the nitrobenzoic acid melting at 138°.

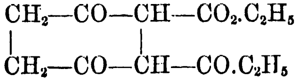
The nitrobenzoic acid thus obtained resembles in melting point and composition an acid obtained by the action of benzoyl chloride on ethyl nitrate, but the latter acid is lemon-yellow, and more freely soluble in water than the former. J. R.

Hippuric Acid and its Derivatives.—By WILLIAM CONRAD (*J. pr. Chem.* [2], xv, 241—260).—That hippuric acid is benzamidoacetic acid, $C_6H_5.CO.NH.CH_2.CO.OH$, is shown by its formation from zinc-glycocine and benzoyl chloride, and from benzamide and monochloracetic acid. A quantity of the acid was prepared from cows' urine by precipitation with hydrochloric acid, and purification of the red powder thus obtained; of the various processes tried for removing the obstinately adherent colouring matter, the best results were obtained by treating the impure acid with nitric acid, whereby the colouring-matters are oxidised (no nitro-hippuric acid being formed), and the addition of stannous chloride to the alkaline solution of the acid, whereby a sort of lake of tin oxide and the colouring-matters is thrown down, the filtrate then giving white hippuric acid with hydrochloric acid. Alkaline hippurates, when treated with ethyl bromide, furnish *ethyl hippurate*, melting at 60·5°, and distilling with partial decomposition at above 180°: the same body results when an alcoholic solution of hippuric acid is allowed to stand for a long time. *Methyl hippurate* is obtained in a similar way; it melts at 80·5°, and cannot be distilled at all. Either of these ethers, when allowed to stand for a long time in contact with alcoholic ammonia, or when warmed with concentrated aqueous ammonia, forms *hippuramide*, melting at 183°: this body is but a weak base, notwithstanding its doubly nitrogenous character; the hydrochloride can be obtained in crystals, but the amide saponifies so readily, that the platinum-salt cannot be formed. No hippuro-nitril could be obtained from the amide by heating alone, or with zinc chloride, phosphoric anhydride, or other water-withdrawing bodies.

When treated with alkaline hypochlorites, hippuric acid readily forms *benzo-glycollic acid*, $C_6H_5.CO.O.CH_2.COOH$, oxygen being substituted for imidogen; a much better yield is thus obtained than by means of Strecker's reaction with nitrous acid, or better nitric oxide; when pure, the crystals melt at almost exactly the same temperature as benzoic acid (120°). Fuming nitric acid dissolves hippuric acid; on gently adding sulphuric acid to the solution, and leaving it for some days at the ordinary temperature in well-closed vessels, so that some pressure may result from liberated gases, *nitro-hippuric acid* is formed;

fuming nitric acid alone, or fuming nitric acid and sulphuric acid without pressure, do not seem to form it so readily. Nitro-hippuric acid, $C_6H_4(NO_2).CO.NH.CH_2.CO.OH$, melts at 162°, and is a strong monobasic acid, forming well-characterised salts; when heated with fuming hydrochloric acid in a cohobator, it readily splits up into glycocine and *meta-nitrobenzoic acid* melting at 141—142°. By treatment with ammonium sulphide and sulphuretted hydrogen, *amido-hippuric* acid is formed; this body melts at 194°; it forms deliquescent, difficultly crystallisable salts with acids, and on heating with hydrochloric acid, breaks up into glycocine and *meta-amidobenzoic acid* melting at 165°; by the action of nitrous acid, it forms, as Griess has shown, *diazo-hippuric acid*, which, when boiled with dilute sulphuric acid, gives rise to *oxy-hippuric acid:* when boiled with concentrated hydrochloric acid, the latter splits up into glycocine and *meta-oxybenzoic acid* melting at 197°. C. R. A. W.

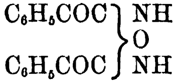
A New Formation of Salicylic Acid. By F. HERRMANN (*Deut. Chem. Ges. Ber.*, x, 646—647).—This acid was obtained, together with ethyl succinylosuccinate, by the action of an excess of sodium on ethyl-succinate, the bodies being left together for months. The formation of salicylic acid under these conditions is easily understood from the constitution of the ether:



$$\begin{array}{l} CH_2—CO—CH—CO_2.C_2H_5 \\ |\qquad\qquad\ | \\ CH_2—CO—CH—CO.C_2H_5 \end{array}$$

C. S.

Phenoxylic Acid. By H. HÜBNER and K. BUCHKA (*Deut. Chem. Ges. Ber.*, x, 479—481).—By heating to 140° in sealed tubes, a mixture of crystallised benzoyl cyanide with glacial acetic acid previously saturated with hydrogen chloride, the authors have obtained a compound agreeing in composition with the formula



$$\left.\begin{array}{l} C_6H_5COC \\ C_6H_5COC \end{array}\right\} \begin{array}{l} NH \\ O \\ NH \end{array}$$

This substance, when heated with aqueous alkalis or hydrochloric acid, yields an acid (phenoxylic), which crystallises in colourless needles, melts at 111°, and forms a crystalline *barium salt* having the formula $(C_6H_5COCOO)_2Ba$.

The barium salt gives, with lead acetate, a white crystalline precipitate of the *lead salt* $(C_6H_5COCOO)_2Pb + H_2O$, which loses water at 160°. J. R.

Polybasic Acids derived from Phenol and Carbon Dioxide. By HERMANN OST (*J. pr. Chem.* [2], xv, 301—316).—Well-dried sodium phenolate is powdered and heated in a suitable vessel in a stream of carbon dioxide, so as to produce basic sodium salicylate; the temperature is then raised to somewhere near 360° (so that paper in the hot air-bath employed is much browned), and the action of the carbon dioxide continued; as the salicylate becomes altered, the temperature may be still further raised, the sodium-salt of the resulting tricarboxylated phenol being much more stable than that of sodium-salicylate. During the first stage, the reaction is—

$$2C_6H_5ONa + CO_2 = C_6H_5.OH + C_6H_4(ONa)(CO.ONa).$$

one-half of the phenol employed distilling over: the latter part of the change is indicated by the equation—

$$2C_6H_4(ONa)(CO.ONa) + CO_2 = C_6H_5.OH + C_6H_2(ONa)(CO.ONa)_3.$$

another quarter of the phenol being again set free: so that the tricarboxylated-phenol produced contains only one-quarter of the phenol originally employed. Dicarboxyl-phenols are also produced by subsidiary reactions in small quantities, but these, for the most part, become further transformed into the tricarboxyl acid. This tricarboxylated acid appears to consist solely of *oxytrimesic acid;* for the purified acid regenerated from the barium-salt yields, on treatment with phosphorus pentachloride, *chlorotrimesic acid,* $C_6H_2Cl(COOH)_3$, from which, by the action of sodium-amalgam, *trimesic acid* results, sublimable at 300°, without previous fusion, and forming an acid barium salt $(C_9H_5O_6)_2Ba.4H_2O$ (Fittig), and an ethyl-salt melting at 133°; the latter is obtained by treating the alcoholic solution of the acid with hydrochloric acid.

By employing a mixture of the phenolates of sodium and potassium (three parts of the first to one of the second), the yield of dicarboxyl-acid is increased, so that from 50 grams of phenol 10—12 of dicarboxyl acid were obtained, 30—32 grams of phenol being recovered by distillation: apparently the dicarboxyl acid is *oxyterephthalic acid,* as it forms a methylic ether melting at 96°, whilst methyl oxyterepthalate synthesized by Burkhardt from terephthalic acid melted at 94°. Its neutral sodium salt, when heated to about 250°, loses carbon dioxide and phenol, and generates the basic salt, $C_6H_3(ONa)(CO.ONa)_2$; at 280—300°, in a current of hydrogen, this latter loses carbon dioxide and forms basic sodium paroxybenzoate, a little tricarboxylated phenol being simultaneously formed. That the dicarboxylated acid may be different from oxyterephthalic acid, however, is rendered not improbable by the circumstance that the author's product split up exactly into phenol and two molecules of carbon dioxide on heating to 200° with concentrated hydrochloric acid; whilst Burkhardt's acid, when similarly treated at 220°, lost only one molecule of carbon dioxide, forming oxybenzoic acid.

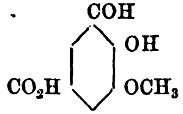
Attempts to prepare higher carboxylated phenols than oxytrimesic acid were fruitless; basic sodium oxytrimesate was heated in a constant stream of carbon dioxide for four days and four nights without forming any tetra-, or higher carboxylated acid: the potassium salt, under the same circumstances, lost a little carbon dioxide, forming some of the dicarboxylated acid. C. R. A. W.

Action of Dehydrating Agents on Anhydrides. By A. MICHAEL and S. GABRIEL (*Deut. Chem. Ges. Ber.*, x, 391—393).—On boiling a mixture of 1 mol. of phthalic anhydride, 2 mols. acetic anhydride, and

1 mol. finely-powdered sodium acetate until the frothing has ceased, pouring the mixture into boiling water and filtering, a solution is obtained depositing, on standing, a yellow precipitate, which, after being purified by boiling with water and treating with animal charcoal, crystallises from alcohol in small, brownish, curved needles melting at 243—246°. This body is *phthalylacetic acid*, $C_4H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CH—CO.OH$.

C. S.

Isomerides of Opianic, Hemipinic, and Quercimeric Acids. By F. TIEMANN and B. MENDELSOHN (*Deut. Chem. Ges. Ber.*, x, 393—402).—Aldehydovanillic acid being at the same time a derivative of protocatechuic acid and salicylic aldehyde, has the following constitution:—



It is isomeric with Beckett and Wright's methylnoropianic acid, which is a derivative of hemipinic acid, containing the carboxyls in the ortho position.

Aldehydovanillic or isomethylnoropianic acid forms alkaline salts dissolving in water with a yellow colour: barium and calcium chloride precipitate the alkaline solution. The copper salt is a green precipitate, dissolving in ammonia with a green colour; the lead salt is white and crystalline; the silver salt is yellowish-white, and reduced by hot water.

When the acid is heated with potash and methyl iodide, its two methyl ethers are formed.

Methyl aldehydovanillate or *isomethyl noropianate*, $C_6H_2\left\{\begin{matrix}CO_2CH_3\\OCH_3\\OH\\COH\end{matrix}\right.$, crystallises in yellow needles melting at 134—135°, and is soluble in dilute alkalis.

Methyl methylaldehydovanillate or *isopianate*, $C_6H_2\left\{\begin{matrix}CO_2CH_3\\(OCH_3)_2\\COH\end{matrix}\right.$, is not soluble in alkalis, and forms small white needles melting at 98—99°, and having an aromatic smell. Hot caustic soda converts it into *isopianic acid*, $C_6H_2\left\{\begin{matrix}CO_2H\\(OCH_3)_2\\COH\end{matrix}\right.$, crystallising from hot water in small white needles, melting at 210—211°. It combines with acid sodium sulphate, and is not coloured by ferric chloride. The salts of the alkali-metals and those of the alkaline earths are soluble in water; the copper salt is a bluish-white, and the lead salt a crystalline white precipitate. The silver salt can be crystallised from hot water.

Isohemipinic acid, $C_6H_2\left\{\begin{matrix}(CO_2H)_2\\(OCH_3)_2\end{matrix}\right.$, is obtained by oxidising a warm aqueous solution of methyl isopianate with a dilute solution of potassium permanganate; by this means methyl isohemipinate melting at 167° is obtained, which on saponifying yields the acid, crystallising from hot water in needles melting at 245—246°. It does not form an anhydride, and can even be sublimed. The salts of the alkalis and alkaline earths crystallise well. The copper, lead, and silver salts resemble those of isopianic acid.

When aldehydo-vanillic acid is heated with hydrochloric acid to 170—180°, it yields, with partial decomposition, *isonoropianic* or *aldehydoprotocatechuic acid*, $C_6H_2\left\{\begin{matrix}CO_2H\\(OH)_2\\COH\end{matrix}\right.$, crystallising from hot water in yellowish needles melting at 240° with decomposition. Alkalis colour the solution yellow, and on heating yellowish-red, and ferric chloride gives a dark green colour, which dilute alkalis change into reddish-violet. It reduces Fehling's solution and ammoniacal silver nitrate. Isonoropianic acid is isomeric with Hlasiwetz's quercimeric acid.

C. S.

Constitution of Quinic Acid. By W. F. HILLEBRAND and R. FITTIG (*Deut. Chem. Ges. Ber.*, x, 523—524).—In order to determine whether all the four oxygen-atoms which the molecule of quinic acid contains, besides the carboxyl group, are present as hydroxyl, Hesse's ethylic ether of quinic acid was heated with excess of anhydrous acetic acid, the excess of acid removed by distillation, and the residue crystallised from water and then from ether. The crystals were found to consist of the ethylic ether of tetracetyl-quinic acid. This ether melts at 135°, and is soluble in hot alcohol and ether. This experiment proves that four alcoholic hydroxyl-atoms are present in quinic acid.

When quinic acid is treated with fuming hydrobromic acid, the chief product of the reaction is benzoic acid, the next protocatechuic acid. As in the case of mucic acid, three molecules of water split off from three molecules of quinic acid. There can be no doubt that quinic acid is the monobasic-pentatomic acid of hexhydrobenzene.

G. T. A.

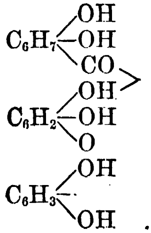
Catechin. By KARL ETTI (*Liebig's Annalen*, clxxxvi, 327—341).—The author prepares catechin by dissolving catechu in eight times its weight of boiling water, straining the liquid through a cloth, and leaving it to stand for some days till the insoluble catechin has subsided. It is then collected in a linen cloth, and submitted to the action of a screw-press. The crude catechin is then dissolved in a sufficient quantity of dilute alcohol, and the solution filtered. It is next shaken up with ether as long as any catechin is dissolved, and after the ether has been removed by distillation, the residue is taken up with distilled water, and the solution is left for a few days, when the catechin crystallises out in an almost colourless state. After pressure in a cloth it is again dissolved in boiling water, when a yellowish-white body remains behind, which is said to be quercetin. To obtain catechin-red (the so-called catechutannic acid), the ether and alcohol are removed by distillation from the intensely red liquid freed from catechin by shaking with ether. On cooling, a red precipitate is thrown down, which may be freed from inorganic bodies by hydrochloric acid. The catechin prepared in the above way precipitates albumin, but not gelatin. Its aqueous solution is not altered by boiling with zinc and sulphuric acid. It does not expel CO_2 from barium carbonate at a boiling heat, but on long continued boiling a small quantity of CO_2 is set free, because the catechin is converted by long boiling into a new compound, which has the power of expelling CO_2 from carbonates.

The results of experiments to free catechin from its water of crystallisation, by standing over sulphuric acid and by drying at 80° to 90°, agreed perfectly with the numbers required by the formula $C_{19}H_{18}O_8$.

By treating catechin with fused potassium hydrate, protocatechuic acid and phloroglucin were obtained. The relation of the formula of catechin to its products of decomposition—

$$C_{19}H_{18}O_8 + 2H_2O = \underset{\text{Protocatechuic acid.}}{C_7H_6O_4} + \underset{\text{Phloroglucin.}}{2C_6H_6O_3} + 4H,$$

and the formation and composition of the derivatives to be described below, appear to indicate that catechin is to be looked upon as the compound of a hitherto unknown tetra-hydrated protocatechuic acid with diphloroglucin, thus:—



$$\begin{array}{l} C_6H_7\begin{cases} OH \\ OH \\ CO \end{cases} \\ C_6H_2\begin{cases} OH \\ OH \\ O \end{cases} \\ C_6H_3\begin{cases} OH \\ OH \end{cases} \end{array}$$

The first anhydride or monoanhydride, $C_{38}H_{34}O_{15} = 2C_{19}H_{18}O_8 - H_2O$, was prepared by drying catechin first over sulphuric acid, then in the air-bath till it lost 2·39 per cent. of water. Catechin red consists of this anhydride.

By treating catechin with sodium carbonate and barium carbonate the following conclusions were arrived at:—

(1.) Catechin does not expel CO_2 from carbonates.

(2.) The monoanhydride behaves towards them like an acid.

(3.) Catechin is quickly changed into its first anhydride by boiling an aqueous solution with sodium carbonate.

The still damp anhydride is moderately soluble in water, but is precipitated by addition of dilute acids. It is very soluble in even dilute alcohol, insoluble in ether. When completely dry, the anhydride behaves indifferently to the above solvents. The solution of the anhydride in water precipitates both albumin and gelatin perfectly; it may therefore properly be named catechu-tannic acid. It forms with alkalis compounds which are soluble in water; with calcium and barium hydrate, insoluble compounds.

The second anhydride or dianhydride, $C_{38}H_{32}O_{14} = 2C_{19}H_{18}O_8 - 2H_2O$, may be prepared by heating the first anhydride up to 162°, or by boiling it for several hours with dilute sulphuric acid. It resembles the monoanhydride in its behaviour to solvents, alkalis, carbonates, albumin, and gelatin. It may be heated to 190° without change, but at 210° it begins to carbonise.

The third anhydride or trianhydride, $C_{38}H_{30}O_{13} = 2C_{19}H_{18}O_8 - 3H_2O$, is prepared by boiling catechin with dilute sulphuric acid. After a time a reddish-yellow precipitate separates out, which when washed and perfectly dried becomes of a dark reddish-brown colour. It is perfectly insoluble in water, alcohol, ether, and potassium hydrate.

The fourth anhydride or tetra-anhydride, $C_{38}H_{28}O_{12} = 2C_{19}H_{18}O_8 - 4H_2O$, prepared by acting for half a day on catechin with concentrated hydrochloric acid in a sealed tube at 160° to 180°. It consists of a dark reddish-brown powder, which resembles the previous anhydride in solubility. It may be heated to 190° without change. When a small quantity was heated to 190° to 210° and treated with dry hydrochloric acid gas, traces of pyrocatechin were obtained.

Behaviour of Catechin to Potassium Hydrate.—When catechin is boiled with a concentrated solution of caustic potash, a body is obtained which differs from the first anhydride only in the amount of its hydrogen. The decomposition is represented by the equation—

$$2C_{19}H_{18}O_8 = C_{38}H_{26}O_{15} + H_2O + 8H.$$

This body behaves towards solvents in the same way as catechin monoanhydride. Its aqueous solution precipitates albumin and gelatin. By the action of fused potash it yields only slight traces of phloroglucin and protocatechuic acid. A dianhydride is obtained by heating this monoanhydride to 165—170°:

$$\underset{\text{Monoanhydride.}}{C_{38}H_{26}O_{15}} - H_2O = \underset{\text{Dianhydride.}}{C_{38}H_{24}O_{14}}.$$

The dianhydride resembles the monoanhydride in its properties.

G. T. A.

On Certain Amides of the Naphthylene-sulphonic Acids.

By J. A. CARLESON (*Bull. Soc. Chim.* [2], xxvii, 360).—The following compounds were obtained by the action of ethylamine, aniline and naphthylamine, on the chlorides of the naphthylenesulphurous acids α and β:—

1. The ethylamide of the acid α is a viscous mass not yet obtained in a crystalline form.

2. The ethylamide of the acid β crystallises in colourless tables, melting point 82·5°. $C_{10}H_7.SO_2.NHC_2H_5$.

3. Anilide of the acid α crystallises in needles, melting at 112°. $C_{10}H_7SO_2.NHC_6H_5$.

4. Anilide of the acid β. Long colourless needles, melting at 132°. $C_{10}H_7SO_2.NHC_6H_5$.

5. Naphthylamide of the acid α. Small needles, melting point 82°. $C_{10}H_7SO_2.NHC_{10}H_7$.

6. Naphthylamide of the acid β. Small elongated needles, melting point 177·5. $C_{10}H_7SO_2.NHC_{10}H_7$. C. L. F.

Phenanthrenequinone. By R. ANSCHUETZ and G. SCHULTZ. (*Deut. Chem. Ges. Ber.*, x, 21).—To avoid fractional distillation with thermometers, the tar residues were first of all freed from water by heating in glazed iron vessels. From these the crystalline masses were easily extracted. The portions used in the following work came over between 310—335°.

Phenanthrene.—Nearly pure phenanthrene is formed on using half the proportion of the oxidation mixture mentioned by Fittig and Ostermayer. Upon treating the mass, after oxidation, with ether, a substance was extracted which proved to be nearly pure phenanthrene.

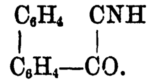
Phenanthrenequinone.—The hydrocarbons boiling between 310—335° were oxidised with potassium dichromate and dilute sulphuric acid. The operation was conducted in a large porcelain basin, the proportions used being 3 litres of equal bulks of oil of vitriol and water, with 300 grams potassium dichromate and 100 grams of the hydrocarbons to be oxidised. When the reaction, which is brisk, has subsided, 300 grams more of potassium dichromate are introduced, and the mixture is gently heated. After cooling, water is added, the liquid is filtered through a linen bag, washing till the liquid runs through colourless. The product of oxidation, which is bright yellow, is dried in a warm place.

It contains the following bodies:—1. Unattacked hydrocarbons; 2. Anthraquinone; 3. Phenanthrenequinone; 4. Diphenic acid; 5. A resinous body, distilling unaltered, soluble in alkaline carbonates.

The oxidation-product is then introduced into concentrated sulphuric acid, left for 12 hours, treated with water, heated to boiling and filtered. The small quantities of diphenic acid and phenanthrenequinone which crystallise out are easily separated by alkalis.

The residue in then treated with sodium carbonate, to remove the remaining diphenic acid and the resinous solid mentioned above, and then purified from the unaltered hydrocarbon with ether. Phenanthrenequinone and anthraquinone, which alone remain, are separated by extracting the former by a very hot solution of acid sodium sulphite. This solution is poured into a mixture of potassium dichromate and dilute sulphuric acid, whereby the phenanthrene-quinone is precipitated as a bright yellow powder. This is subsequently purified by crystallising from alcohol.

Action of Ammonia on Phenanthrene-quinone.—If to a hot solution of phenanthrenequinone ammonia be added, long yellow needles crystallise out on cooling, having the composition (probably)—



$$\begin{array}{ll} C_6H_4 & CNH \\ | & | \\ C_6H_4\text{—} & CO. \end{array}$$

The reaction may be expressed by the following formula:—

$$C_{14}H_8O_2 + NH_3 = C_{14}H_9NO + H_2O.$$

Phenanthrenequinonimide melts at 147° : dissolves in oil of vitriol with a red colour, yielding phenanthrenequinone on the addition of water. Hydrochloric acid forms at first a red solution, and finally decomposes it into ammonia and phenanthrenequinone.

On analysis, it was found that 0·3083 grm. of substance yielded only 0·3067 grm. phenanthrenequinone, instead of the calculated 0·3099. A nitrogen determination with soda lime gave 5·42 per cent. only. This arises from the formation on heating with soda-lime, of a needle-like nitrogenous body, which had not undergone decomposition. This will be referred to later on. When alcoholic ammonia is heated under pressure with phenanthrenequinone, at first phenanthrenequinonimide is formed, but after the process has been continued for a day or two, a fine-grained substance of a crystalline character is formed, bearing, in its behaviour to solvents, a great resemblance to the acetylchrysophanamide, described by Liebermann. It dissolves in concentrated sulphuric acid with a fine blue colour. Water precipitates it unaltered. The addition of alcohol to the solution in sulphuric acid produces a green colour, which dyes silk. On heating the sulphuric acid solution for some time, and adding water, a dirty gray precipitate is formed. This sublimes unaltered on heating in long colourless needles. It contains nitrogen, and bears some resemblance to carbazol, being identical with the white sublimate mentioned above. Its melting point lay over 320°, and therefore could not be determined. Concentrated sulphuric acid colours it red at first, dissolving it subsequently with a splendid blue colour.

With chloride of aniline phenanthrene-quinone yields colouring matters now under examination. C. L. F.

A New Acid from Phenanthrene-quinone. By P. FRIEDLANDER (*Deut. Chem. Ges. Ber.*, x, 534—537).—Commercial phenanthrenequinone is boiled with caustic soda, the water which evaporates being replaced, till the greater part is dissolved to a dark brown liquid. On addition of hydrochloric acid to the diluted and filtered solution, diphenyleneglycollic acid is precipitated in brownish crystals. This acid, when purified, consists of brilliant white laminæ, which melt at 162°, and are easily soluble in hot water and the ordinary solvents. The formula of the acid is $C_{14}H_{10}O_3$. Its salts with the alkalis are very soluble, those with the alkaline earths less so, and those with the heavy metals are insoluble in water. The ethylic ether, $C_{14}H_9O_3C_2H_5$, may be obtained by passing hydrochloric acid into a warm alcoholic solution of the acid. It crystallises in small hard prisms, which melt at 92°. Phenyleneglycollic acid loses carbon dioxide and water when it is heated above its melting point, and yields Barbier's fluorenic ether (*this Journal*, 1876, ii, 77). The same body is also obtained by warming the acid with concentrated sulphuric acid, and precipitating with water.

Fluorenic alcohol is prepared by heating the sodium salt of diphenyleneglycollic acid to 120°, or better by heating the aqueous solution of the sodium salt with excess of caustic soda in a sealed tube to 160°. This body is identical with the fluorenic alcohol obtained by Barbier (this *Journal*, 1876, ii, 77) from diphenyleneketone. It is almost insoluble in cold water, but dissolves easily in alcohol, ether, and benzene; crystallises from the last-named solvent in fine hexagonal plates, which melt at 151—152°.

Diphenyleneketone.—Chromic acid mixture attacks diphenyleneglycollic acid at a gentle heat, chlorine is given off, and a yellow body insoluble in water and caustic soda, which crystallises from alcohol in yellow needles, melting at 82°, remains behind. This is diphenyleneketone.

Diphenylene-acetic acid is obtained by heating diphenyleneglycollic acid with concentrated hydriodic acid and amorphous phosphorus in sealed tubes to 140°. It dissolves in benzene, ether, and alcohol, and forms small imperfect crystals, which melt at 220—222°. This body may also be called *fluorene-carbonic acid*. By passing hydrochloric acid into a boiling alcoholic solution of this body, the ethyl ether is formed in small hard crystals which melt at 165°. When fluorene carbonic acid is heated to above its melting point, it is partly decomposed into carbon dioxide and fluorene.

Dibromodiphenylene-glycollic acid is prepared by addition of bromine, with constant stirring, to diphenyleneglycollic acid suspended in water.

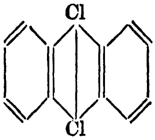
It is soluble in alcohol, ether, and acetic acid, and crystallises in small complex needles, which melt at about 225°. The ethyl ether formed by the action of hydrochloric acid consists of small brilliant prisms, which melt at 150—151°.

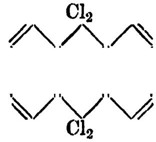
Dibromodiphenyleneketonic acid splits up, under the action of chromic acid mixture, into carbon dioxide and dibromodiphenylene ketone.

G. T. A.

Halogen-Derivatives of Anthracene. By F. SCHWARZER (*Deut. Chem. Ges. Ber.*, x, 376—379).—*Dichloranthracene tetrabromide* is obtained by exposing dichloranthracene to bromine vapour for some time. It is sparingly soluble in alcohol and ether, freely in chloroform and benzene, and crystallises in white silky needles melting at 166°. On heating it to 180—190°, *dichloromonobromanthracene* is formed, while alcoholic potash converts it into *dichlorodibromanthracene.* The former, $C_{14}H_7Cl_2Br$, crystallises from benzene in greenish-yellow plates melting at 168°; the latter $C_{14}H_6Cl_2Br_2$ forms small yellowish needles melting at 251—252°.

Dichloranthracene dichloride, $C_{14}H_8Cl_2.Cl_2$, is readily formed by passing chlorine into a solution of anthracene in chloroform. It crystallises in transparent prisms melting at 149—150°, and freely soluble in benzene and chloroform, but only sparingly in alcohol and ether. On heating it to 170° it yields trichloranthracene and a little dichloranthracene; the same decomposition takes place gradually at the common temperature, even if the compound be kept in an atmosphere of hydrochloric acid. $C_{14}H_7Cl_3$ crystallises from alcohol in long yellow needles melting at 162—163°. On heating the dichloride with water or alcoholic potash, it is converted into *anthraquinone*. Concentrated sulphuric acid produces the same reaction in the cold; dichloranthracene dichloride is consequently the chloride of anthraquinone, and the constitution of dichloranthracene and its dichloride may be expressed as follows:—





C. S.

Action of Chromyl Dichloride on Anthracene. By A. HALLER (*Compt. rend.*, lxxxiv, 558—559).—The product of the action of chromyl chloride on anthracene dissolved in glacial acetic acid is anthraquinone. The author is about to investigate the action of this body on camphor and on the aromatic amines. W. R.

Reduction-products of Quinizarin. By C. LIEBERMANN and F. GIESSEL (*Deut. Chem. Ges. Ber.*, x, 606—611).—Quinizarin was obtained by heating equal numbers of molecules of phthalic anhydride and parachlorophenol with sulphuric acid equal to ten times the weight of the latter to 210° for some hours. In this way 8—10 per cent. of the chlorophenol is converted into quinizarin; at the same time some purpurin is formed which can be easily separated, as quinizarin is almost insoluble in a cold solution of sodium carbonate.

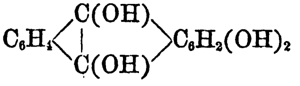
On boiling quinizarin with dilute hydriodic acid and phosphorus, or heating it with hydrochloric acid and stannous chloride, it is reduced to *hydroquinizarin*, $C_{14}H_{10}O_4$, crystallising from alcohol in yellow needles. It forms an insoluble yellow barium salt, and its alkaline, yellow fluorescent solution readily absorbs oxygen, quinizarin being reproduced. Sometimes if the reaction is carried on longer it goes further, *quinizarol*, $C_{14}H_{12}O_3$ being formed, which resembles hydroquinizarin.

When quinizarin is boiled for an hour with hydriodic acid of sp. gr. 1·8, and an excess of phosphorus, it yields *hydroanthracene hydroquinone*, $C_{14}H_{12}O_2$, which is readily soluble in alcohol, ether and acetic acid, and crystallises in yellowish-white rhombic plates, melting at 99°; its solutions show a strong greenish-yellow fluorescence; it volatilises with steam; the alcoholic solution is coloured green by ferric chloride. It forms a crystalline potassium salt, $C_{14}H_{11}O_2K$, and insoluble yellow lead and copper salts, which are obtained by precipitating the alcoholic solution containing a little ammonia with the corresponding acetates, the lead compound $(C_{14}H_{10}O_2)_2Pb$ forms microscopic needles. On heating the hydroquinone with a mixture of acetyl chloride and acetic anhydride, the compound $C_{14}H_{11}O_2.C_2H_3O$ is obtained, forming pale yellow warty crystals, melting at 136—138°.

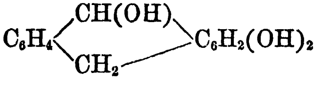
An ammonia-compound could not be obtained, but ethylamine acts readily on the hydroquinone, yielding $C_{14}H_{10}\left\{\begin{matrix}OH\\NH(C_2H_5)\end{matrix}\right\}$ which crystallises in lemon-yellow, silky needles, melting at 162° and decomposed by boiling alkalis. When the hydroquinone is boiled with acetic acid, manganese dioxide, and sulphuric acid, it is oxidised to $C_{14}H_8O_3$ which crystallises in orange-coloured needles melting at 191°.

The constitution of these compounds is expressed by the formulæ—

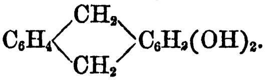
Hydroquinizarin.



Quinizarol.



Hydroanthracenehydroquinone.



C. S.

The Constitution of Pseudopurpurin. By A. Rosenstiehl (*Compt. rend.*, lxxxiv, 559—562).—From the results obtained by Schunck and Römer the author has been led to modify his theory as to the method of formation of purpurin and the yellow substance which accompanies it. This substance is evidently the one he named ε-purpurin, and the formula given by the above chemists, viz., $C_{15}H_8O_6$, is doubtless correct. When heated, it yields purpuroxanthin, thus: $C_{15}H_8O_6 = C_{14}H_8O_4 + CO_2$. Schunck and Römer believe it to be an oxidation-product of a more complex substance accompanying purpurin.

Schützenberger and Schiffert found pseudopurpurin to contain two atoms of oxygen more than purpurin, and after Graebe and Liebermann had discovered the true formula of alizarin, they gave that of pseudopurpurin as $C_{14}H_8O_6$. The author attempted to prepare pseudopurpurin from the sulphonic derivative of purpurin by fusion with potash, but without success. He next converted some purpurin by heating it to 180°, and measured the amount of carbonic anhydride which was regularly evolved. He found numbers agreeing with the equation—

$$\underset{\text{Pseudopurpurin.}}{C_{15}H_8O_7} = CO_2 + \underset{\text{Purpurin.}}{C_{14}H_8O_5}.$$

The calculated composition of $C_{15}H_8O_7$ does not differ greatly from the results of Schützenberger and Schiffert's analyses.

If the above formula for pseudopurpurin is the correct one, it should bear the same relation to madder-orange that purpurin bears to purpuroxanthin, viz. :—

$$\underset{\text{Pseudopurpurin.}}{C_{15}H_8O_7} - O = \underset{\text{Madder-orange.}}{C_{15}H_8O_6}.$$

$$\underset{\text{Purpurin.}}{C_{14}H_8O_5} - O = \underset{\text{Purpuroxanthin.}}{C_{14}H_8O_4}.$$

This formula also explains the conversion of pseudo-purpurin into purpurin by cold alkali, as well as the formation of all colouring matters found in madder (except alizarin) by its decomposition.

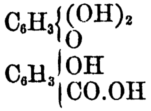
W. R.

Madder Colours. By H. PLATH (*Deut. Chem. Ges. Ber.*, x, 614—617).—When pseudopurpurin, $C_{14}H_8O_6$, is heated with acetic anhydride to 180°, it is converted into triacetyl-purpurin. When sublimed purpurin is crystallised from dilute alcohol, Wolff and Strecker's hydrate, $C_{14}H_8O_5 + H_2O$, is obtained in slender orange-coloured needles; this body is quite different from pseudopurpurin, and does not lose its water of crystallisation completely till heated to 160°. On heating dibromanthrapurpurin with concentrated sulphuric acid to 200°, it is converted into monobromopurpurin, which is also formed by adding an excess of bromine to a solution of purpurin in glacial acetic acid; it dyes mordants like purpurin. When one of these bromine compounds is fused with potash, no pseudopurpurin is formed, but a body which seems to be only impure purpurin. On heating pseudo-purpurin with water to 200°, it yields carbon dioxide and purpurin.

Xanthopurpurin-carbonic acid is readily obtained by suspending crude purpurin in acetic acid, adding a few drops of fuming nitric acid and heating to the boiling point. On cooling the solution slowly and adding water, xanthopurpurin-carbonic acid is precipitated. From this it appears that this acid is not contained in crude purpurin, but is produced by its oxidation; under the same conditions pseudopurpurin yields the same compound, but not so readily.

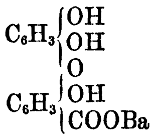
C. S.

Maclurin. By R. BENEDIKT (*Liebig's Annalen*, clxxxv, 114—119).—Maclurin is best prepared from the muddy sediment deposited in the extraction of fustic, by treating it with dilute hydrochloric acid, and crystallising it several times from hot water after removal of the liquid by pressure. The formula assigned to this body by the author is—

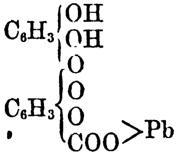


$$\begin{array}{l} C_6H_3\left\{\begin{matrix}(OH)_2\\ O\end{matrix}\right. \\ C_6H_3\left\{\begin{matrix}OH\\ CO.OH\end{matrix}\right. \end{array}$$

and those of the three known salts are—

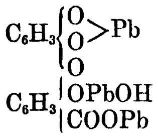


$$\begin{array}{l} C_6H_3\left\{\begin{matrix}OH\\ OH\\ O\end{matrix}\right. \\ C_6H_3\left\{\begin{matrix}OH\\ COOBa\end{matrix}\right. \end{array}$$



$$\begin{array}{l} C_6H_3\left\{\begin{matrix}OH\\ OH\\ O\end{matrix}\right. \\ C_6H_3\left\{\begin{matrix}O\\ O\\ COO\end{matrix}\right.\!\!>Pb \end{array}$$

Lead salt of Hlasiwetz.



$$\begin{array}{l} C_6H_3\left\{\begin{matrix}O\\ O\end{matrix}\!>Pb\right. \\ \quad\;\; O \\ C_6H_3\left\{\begin{matrix}OPbOH\\ COOPb\end{matrix}\right. \end{array}$$

Lead salt of Löwe.

Bromomaclurin ($C_{13}H_7Br_3O_6 + H_2O$) is prepared by adding bromine with constant stirring to maclurin, kept under water, in proportion of three molecules to one, and extracting the product several times with boiling water. It may be purified by solution in alcohol and precipitation with a weak acid.

Maclurin is decomposed by the action of dilute sulphuric acid at 120° into protocatechuic acid and phloroglucin. If the sulphuric acid is replaced by concentrated hydrochloric acid, protocatechuic acid is obtained, together with a small quantity of a red body which is probably rufimoric acid, and the phloroglucin is converted into diphloroglucin.

Hlasiwetz having described the preparation of α-phloretin by fusing together phloroglucin and phloretic acid, the author endeavoured to obtain a corresponding α-maclurin. The product of the reaction, besides unchanged phloroglucin and protocatechuic acid, consisted of a body which crystallised in laminæ from boiling water, and was easily decolorised by animal charcoal.

The great similarity of these crystals and of α-phloretin to diphloroglucin, and the fact that phloroglucin when heated for a long time to above its melting point is converted into diphloroglucin, show that the three bodies, α-phloretin, α-maclurin, and diphloroglucin, are identical. This supposition is fully confirmed by analysis. G. T. A.

Retene and some of its Derivatives. By A. G. EKSTRAND (*Liebig's Annalen*, clxxxv, 75—113).—When wood-tar is distilled, a thick oil passes over towards the end of the operation, solidifying on cooling to a granular mass, which is called tar-tallow, and used for lubricating mixtures. The substance contains a large proportion of retene, which is isolated by pressing the mass at a low temperature, first between cloth and then repeatedly between filter-paper. After washing with ether and crystallising several times from alcohol, pure retene, $C_{18}H_{18}$, is obtained in large plates resembling mica, and melting at 98·5°. The specific gravity of the solid is about 1·1, and of the liquid 1·08; 100 parts of alcohol dissolve at the boiling point 69, and at the common temperature 3 parts. It dissolves readily in hot glacial acetic acid, petroleum-naphtha, carbon sulphide, benzene, and ether. It sublimes readily but becomes brown when heated continually in the air.

Retene-picric acid, $C_{18}H_{18} + C_6H_2(NO_2)_3OH$, crystallises from alcohol in glistening yellow or orange needles melting at 123—124°.

Retene does not combine with nascent hydrogen. Chlorine converts it first into a dichloride, which is very unstable, and seems to be easily transformed into monochlororetene.

Dibromoretene, $C_{18}H_{16}Br_2$, is obtained, but only in small quantity, by adding bromine to retene in the presence of water. It crystallises from hot petroleum-naphtha in glistening plates melting at 180°.

Tetrabromoretene, $C_{18}H_{14}Br_4$, is formed by acting on retene with an excess of bromine and heating on a water-bath. It is insoluble in alcohol, sparingly soluble in ether and glacial acetic acid, more freely in petroleum-naphtha, and crystallises from hot benzene or carbon sulphide in colourless prisms melting at 210—212°. It seems to combine with bromine to a dibromide, forming a viscid yellow mass, which when heated with alcoholic potash is converted into a brown body, separating from carbon sulphide as a glassy mass having the composition of tetrabromoretene.

Retenedisulphonic acid, $C_{18}H_{16}(SO_3H)_2$. When retene is gradually added to a mixture of equal volumes of concentrated and fuming sulphuric acid, and the liquid left to itself for 2—3 weeks, slender needles of Fritzsche's compound, $C_{18}H_{16}(SO_3H)_2 + 5H_2SO_4$, separate out. The free disulphonic acid obtained from the barium or lead salt is very soluble, and separates from a concentrated aqueous solution in small needles and from glacial acetic acid in well defined needles or prisms. Its concentrated aqueous solution is precipitated by sulphuric acid; and the compound thus formed seems to contain varying quantities of the latter acid. The following salts were prepared and analysed:—

				1 part dissolves
$C_{18}H_{16}(SO_3K)_2$	+	$\frac{1}{2}H_2O$ (at 100°),	silky needles,	in 5—6 of water
$C_{18}H_{16}(SO_3Na)_2$	+	$\frac{1}{2}H_2O$ „	„	in 2—3 „
$C_{18}H_{16}(SO_3)_2Ba$	+	H_2O „ $6H_2O$ (at 15°)	prisms, slowly	in 60—61 „
$C_{18}H_{16}(SO_3)_2Sr$	+	$1\frac{1}{2}H_2O$ (at 100°)	„	in 24—25 „
$C_{18}H_{16}(SO_3)_2Ca$	+	$1\frac{1}{2}H_2O$ „ $8H_2O$ (at 15°)	„	in 20—21 „
$C_{18}H_{16}(SO_3)_2Mg$	+	$2H_2O$ (at 100°),	woolly needles,	in 25—26 „
$C_{18}H_{16}(SO_3)_2Cu$	+	$1\frac{1}{2}H_2O$ „ $5H_2O$ (at 15°)	pale green long needles	in 3—4 „
$C_{18}H_{16}(SO_3)_2Pb$	+	H_2O (at 100°),	long prisms, slowly	in 54—55 „

Retenedisulphonic dichloride, $C_{18}H_{16}(SO_2Cl)_2$, is obtained by the action of phosphorus pentachloride on the potassium salt. It crystallises from hot glacial acetic acid in hard prisms, melting at 175°; it readily dissolves in benzene, sparingly in ether, and is hardly attacked by boiling water, which decomposes it only completely at 160°.

An isomeric retenedisulphonic acid appears to exist.

Retenetrisulphonic acid, $C_{18}H_{15}(SO_3H)_3$, is formed by heating retene with a mixture of common and fuming sulphuric acid on a water-bath; it is readily soluble in water; its solution is not precipitated by sulphuric acid. As the salts show, this acid is probably a mixture.

The vapour of retene is not changed by passing over heated lead oxide.

Dioxyretistene, $C_{16}H_{14}O_2$, is formed by oxidising the hydrocarbon with chromic acid. It crystallises from hot alcohol in flat orange prisms melting at 190°, and dissolving readily in hot benzene and glacial acetic acid. In cold alcohol, ether, and petroleum-naphtha it is sparingly soluble. It is also soluble in acid sodium sulphite. By the action of bromine a compound having the empirical formula $C_{40}H_{31}Br_4O_5$(?) was formed, crystallising from hot acetic acid in small prisms melting at 234—235°.

When dioxyretistene is heated with baryta, a red oil distils which solidifies on standing; the crystals separate from alcohol in flat yellow prisms, melting at 89—90°; its composition is $C_{22}H_{22}O$. Besides this body a pale yellow oil boiling at 215—220° and consisting of C_7H_8 is formed. Dioxyretistene is not reduced by sulphur dioxide, but yields a yellow solution with zinc-dust in presence of an alkali. On heating it with zinc-dust, the hydrocarbon, $C_{14}H_{14}$, of Wahlfors is obtained, which melts at 56—57°, and does not combine with picric acid, at the same time much retene is obtained. The retistene of Wahlfors was probably a mixture of these two hydrocarbons.

When retene is oxidised by a solution of chromic acid, a soluble body is also formed. It is obtained from hot dilute alcohol in well defined crystals melting at 139°. It is an acid having the composition $C_{16}H_{16}O_3$.

$C_{16}H_{15}NaO_3$ crystallises in pale yellow plates or scales. $(C_{16}H_{15}O_3)_2Ba$ forms large colourless plates. The lead and silver salts are white precipitates.

Another acid, $C_{18}H_{16}O_2$, which is also formed, crystallises from alcohol in pale yellow or colourless needles, melting at 222°. $C_{18}H_{15}NaO_2$ forms large, yellowish-brown plates, and dissolves freely in water. The barium-salt is sparingly soluble and forms shining scales.

Both compounds are obtained in small quantities only. C. S.

Note on the Action of Dilute Nitric Acid on Brucine.

By W. A. SHENSTONE (*Pharm. J. Trans.* [3], vii, 652).—The experiments were undertaken with the view of settling the question as to whether brucine when acted on by nitric acid yields strychnine or not. Brucine, when heated on a water-bath with 1 part of nitric acid and 9 parts of water, yields strychnine, when the experiment is performed as above; but on evaporating over the bath, only slight evidence of strychnine was obtained. Using acid of half the strength of that employed in the first experiment, crystals of strychnine in some quantity were obtained. In all these experiments carbonic anhydride was given off, and a yellow resin produced. In another series of experiments on specially prepared brucine, strychnine was generally formed, the quantity depending on the strength of acid employed, the stronger acid appearing to be prejudicial to the formation of strychnine. With brucine prepared by the author, little or no strychnine could be formed. Brucine adulterated with 0·1 per cent. of strychnine, and digested with a 5 per cent. solution of nitric acid, gave no reaction for strychnine, the fact, therefore, of not finding strychnine in brucine by acting with nitric acid, is no proof of its purity. E. W. P.

Studies on the Chinoline Series; Transformation of Chinoline into Aniline.

By J. DEWAR (*Proc. Roy. Soc.*, xxvi, 65—71), (*Compt. rend.*, lxxxiv, 611—614).—This paper is in further support of the theoretical relations between the members of the pyridine and chinoline series. It was important to ascertain if the members of the chinoline series yielded an acid on oxidation. By oxidation with potassium permanganate a well defined acid was obtained, viz., *leucolinic acid*, $C_9H_9NO_3$.

The acid may be regarded as formed by one of two reactions—

$$\begin{aligned} a.\ & C_9H_7N + O_2 + H_2O = C_9H_9NO_3 \\ b.\ & C_{10}H_9N + O_5 = C_9H_9NO_3 + CO_2. \end{aligned}$$

Its salts are mostly soluble, except the lead, mercurous, and ferric salts.

Decompositions.—*Heat* gives an oily sublimate, which probably contains the anhydride, as when boiled with water it regenerates the acid.

Soda-lime.—The acid heated with soda-lime to a low red heat, leaves a deposit of carbon, and yields an alkaline, oily distillate, soluble in dilute hydrochloric acid, and reacting like pyrrol. The solution when evaporated leaves hydrochlorides of the bases, which, after being freed from pyrrol, were heated with potash, when the bases distilled as a colourless oil. This oil has all the physical and chemical characters of pure aniline, the only substance associated with the aniline being ammonia.

The acid heated with potash-lime gave no pyrrol, the reaction being—

$$C_9H_9NO_3 = C_6H_7N + CO_2 + H_2O + C_2.$$

If the potassium salt be fused with excess of potash, ammonia is evolved, and salicylic acid is found in solution.

A solution of the acid in glycerin gave a distillate of glycerin, aniline, and small quantities of a substance having the characters of indol.

The relations of chinoline, leucoline, and indol will be investigated hereafter.
F. J. L.

Extraction of Caffeine. By LEGRIP and PETIT (*Bull. Soc. Chim.* [2], xxvii, 290).—After having tried various methods for the extraction of caffeine, particularly that recently recommended by Cazeneuve and Caillol, the authors have adopted the following, as giving the best results. Coarsely powdered tea is covered with twice its weight of boiling water, left for a short time at a gentle heat, and the resulting moist powder exhausted with chloroform. When the latter is colourless, the exhaustion is complete. On distillation of the chloroform extract, an oily residue and caffeine remain in the retort. On treating this residue with a suitable amount of boiling water containing a small quantity of animal charcoal, then filtering and cooling, magnificent crystals of caffeine are obtained. The tannin is retained by the water, the caffeine being dissolved in the chloroform. No satisfactory results were obtained by treating the powdered tea directly with the chloroform.
C. L. F.

Glycyrrhizin. By J. HABERMANN (*Deut. Chem. Ges. Ber.*, x, 870—871).—Amorphous, commercial glycyrrhizin yields to glacial acetic acid a body, crystallising from alcohol in prismatic needles, which are grouped in hemispherical masses. It dissolves readily in water or spirits of wine, less freely in absolute alcohol, and hardly in ether. In its reactions it resembles Gorup-Besanez's amorphous compound, but its composition is different, and on boiling it with dilute sulphuric acid, a resinous body is formed, having the sweet and acrid taste of the original substance. C. S.

Note on Dikamali Resin. By FLÜCKIGER (*Pharm. J. Trans.*, [3], vii, 589).—The resin known in India under the name of dikamali, has a well marked odour, and is yellow when powdered, and dissolves with yellow colour in alcohol (0·83 sp. gr.), the solution having a fine yellow colour, with a well marked greenish hue. It is neutral to litmus paper, but is coloured intensely greenish-brown by ferric chloride. Fused with caustic potash it yields a substance from which protocatechuic acid separates on addition of acid. On exhausting the resin with hot alcohol, gardenin is obtained in yellow acicular crystals, melting at 155°; these crystals appear to have the formula, $C_{23}H_{30}O_{10}$. The amorphous portion of dikamali is also soluble in alcohol, and yields with lead acetate a yellow precipitate, lead also remaining combined in solution.

The precipitate on decomposition yielded a quantity of resin, too small for examination, whereas the solution appeared to contain a resin melting below 100°, and answering to the formula, $C_{23}H_{34}O_4$, but the analytical numbers were not very satisfactory. E. W. P.

Note.—Stenhouse (*Chem. Soc. J.*, 1877, i, 551) is of opinion that $C_5H_5O_2$ represents the constitution of *gardenin* more correctly than Flückiger's formula.

Active Principle of the Strophantus Hispidus. By E. HARDY and N. GALLOIS (*Compt. rend.*, lxxxiv, 261—263).—The arrow poison of the Pahouins, variously termed *Inée*, *Onaye*, or *Goubi*, is derived from the *Strophantus hispidus*, a plant belonging to the apocynaceous order. The active principle, which has not been hitherto isolated, was obtained by treating the decorticated seeds with alcohol, slightly acidulated with hydrochloric acid. The alcoholic solution was evaporated to the consistence of an extract, and then taken up with cold water. The solution thus obtained yielded on spontaneous evaporation brilliant white crystals, which were purified by a second crystallisation. The crystals, which are highly poisonous, are soluble in cold water and alcohol, but very slightly so in ether and chloroform. Their aqueous solution is not precipitated by any of the reagents which precipitate alkaloïds, such as the double iodide of potassium and mercury, phosphomolybdic acid, or the chlorides of gold and platinum. Neither does it reduce Fehling's solution after boiling with dilute sulphuric acid.

It is proposed to name this active principle *strophantine.*

The integuments of the seeds treated in a similar manner also furnished a crystallisable substance, which, unlike the previously mentioned principle, gave the usual reactions of an alkaloïd with the foregoing precipitants; however, its physiological properties proved to be very different from those of strophantine, for when injected in considerable quantity beneath the skin of a frog, it did not arrest the movements of the heart.

The alkaloïd from the integuments (or pericarps ?) has been termed *inéine.* J. W.

On the Pectin Group. By E. REICHARDT (*Arch. Pharm.* [3], x, 116—120).—This paper is a critical examination of the results obtained in previous investigation with regard to the formula of the group of pectin bodies. It is not fitted for abstraction. E. N.

Colouring Matter of the Petals of Rosa Gallica. By HAROLD SENIER (*Pharm. J. Trans.* [3], vii, 650).—The petals were digested with ether, and the solution filtered, by which means quercetin and fat were removed. Alcohol was found best to extract the colour, producing a colourless solution, which reddens with age; the aqueous extract is, however, coloured. From the alcoholic solution, the colouring matter was precipitated green by lead acetate: it was then washed and dried, and decomposed in the one case by sulphuretted hydrogen; in the other by sulphuric acid, and then yielded a bright red solution. Dilute acids deepen the colour; alkalis change it to a deep red, with a green fluorescence; potash, soda, and ammonia yield crystalline compounds; fine octohedrons were obtained, when potash and soda were both employed. Alkaline carbonates act in the same manner as the alkalis, except that the change of colour is accompanied by effervescence. Sulphuretted hydrogen changes the red to a brown, and stannic chloride from red to dark magenta; on boiling with metallic mercury, a dark violet is produced; mercuric nitrate and chloride give a white or pinkish precipitate; barium and calcium hydrate a yellowish-green precipitate, turning brown when dry. The red colouring matter in solution has an acid reaction, and is not altered by hydrogen peroxide. The lead salt appeared by analysis to consist of $Pb_2C_{21}H_{29}O_{30}$. Dissolved in alcohol, the extract gives absorption bands, of which a sketch is given in the paper. With a solution rendered acid by sulphuric acid, absorption takes place between D and F, having its maximum about half way between E and F. A solution rendered alkaline by ammonia absorbs light partially between *a* and *c*, and from G to beyond H; and a solution treated with stannic chloride absorbs light from B to G. E. W. P.

Physiological Chemistry.

On the Respiration of the Mammalian Fœtus. By N. ZUNTZ (*Pflüger's Arch. f. Physiologie*, xiv, 605—627).—The author maintains, with Pflüger, and in opposition to Zweifel, that the fœtus takes up a very small quantity of oxygen. He thinks it probable that the albumin of the fœtus is partly formed from peptones, and is partly taken up as such from the maternal blood, or from the utricular glands. Zweifel found that shortly after the death of the mother by asphyxia, the blood in the umbilical vessels became black, and dyspnœa of the fœtus occurred; this he attributed to consumption of its oxygen by the fœtus. The author confirms the fact, but explains it differently, as will be seen from the following conclusions, which he draws from an experiment of this nature made on a Guinea pig:—

1. On the occurrence of asphyxia in the mother, the fœtus loses oxygen in the placenta, giving it up to the asphyxiated maternal blood, instead of absorbing oxygen, as is shown by the darker colour of the blood in the umbilical vein.

2. If the blood of the fœtus has become arterial in consequence of its own respiration, the muscular substance of the uterus, which is no longer traversed by its blood, and is poor in oxygen, can abstract very considerable quantities of oxygen from the fœtal blood.

The proof of the fact that the fœtus has a smaller consumption of oxygen than the adult, the author gives as follows:—Closure of the umbilical vessels, *i.e.*, stoppage of the access of oxygen, is borne much longer than occlusion of the trachea after birth, whereas the fœtus becomes asphyxiated almost as rapidly as its mother, when the latter robs it of its oxygen (Zweifel).

From the latter fact it follows that the fœtus, after its blood has lost all its oxygen, becomes asphyxiated almost as rapidly as its mother, and that after arrest of the interchange of gases, it lives much longer than an adult animal, only because it takes so much longer to consume its store of oxygen, which in proportion to its body-weight is even smaller.

Although no certain conclusions with regard to the consumption of oxygen can be drawn from the difference in colour of the blood in the umbilical cord, the author is of opinion that the slightness of the difference in colour between the venous and the arterial blood of the cord, render the smallness of the process of oxidation in the fœtus highly probable.

The author further contends that if the small difference in pressure (calculated at 7·6 mm. of mercury) suffices to increase the content of oxygen in the blood by several parts per cent. during its passage through the placental capillaries, there can be no difficulty in supposing that the much greater difference between the pressure in the blood-capillaries and the tissues generally causes 6 to 8 parts per cent. of oxygen to pass over into the latter. Any assumption of a specific secretory function as causing the passage of oxygen from the maternal to the fœtal blood is disproved by the fact, frequently observed by the author, that the current of oxygen is immediately reversed if the tension of the fœtal is greater than that of the maternal blood.

E. C. B.

Physiology of Carbohydrates. By OTTO NASSE (*Pflüger's Archiv. f. Physiologie*, xiv, 473—484).—From the year 1831, when Leuchs discovered the chemical action of saliva on starch, up to the present day, dextrin has always been regarded as the product of the action. It is now found, however, that this supposition cannot hold good, as the substance formed does not reduce Barfoed's solution, which reagent, consisting of a dilute solution of neutral cupric acetate in acetic acid, is easily reduced by dextrin, though not by such sugars as lactose and maltose, which reduce cupric salts in the presence of alkalis.

The substance thus formed by the action of saliva on starch, which has hitherto been unobserved, may be termed *Ptyalose* (saliva sugar), or better, *Amylum ptyalose*. No crystals having as yet been obtained, so that its purity could not be guaranteed, it has not been analysed, nor its rotatory power estimated. A carefully prepared solution, however, showed this distinctive characteristic, that on boiling with sulphuric acid, its reducing power was doubled.

Besides ptyalose, achroodextrin was also formed by the action of saliva on starch. As the reducing power of this substance gradually decreases by repeated digestion with alcohol, it probably depends entirely on mechanically admixed ptyalose, so that pure achroodextrin may possibly possess no reducing power.

Experiments were next made as to the action of saliva on glycogen. Two kinds of glycogen were used: 1, an old preparation of liver-glycogen, from different animals; and 2, muscle-glycogen, from dogs. Glucose was not found amongst the products, but only achroodextrin and ptyalose, or glycogen-ptyalose, the reducing power of which was doubled by boiling with dilute sulphuric acid. The identity of these results, compared with which the slight differences hitherto noticed between the two kinds of glycogen are insignificant, proves that the glycogen of the liver is the same as that of the muscles.

The different muscles were found to contain very varying quantities of glycogen, those muscles containing the least which were most active before the death of the animal. F. J. L.

Formation of Phenol in the Animal Body. By E. SALKOWSKI (*Deut. Chem. Ges. Ber.*, x, 842—844).—On passing ligatures round the intestines of dogs which did not previously excrete phenol in their urine, phenylsulphuric acid and indican appeared in 24—36 hours, one dog secreting in 24 hours a quantity equivalent to 0·249 tribromophenol. It appears, however, doubtful, whether the stagnation of the contents of the bowels is the sole condition for the formation of larger quantities of the above compounds. Human urine rich in indican always contains much phenol. Two dogs, which after the above operation secreted much phenol, did not produce any more after the establishment of a biliary fistula. C. S.

Presence of Zinc in the Bodies of Animals and Plants. By G. LECHARTIER and F. BELLAMY (*Compt. rend.*, lxxxiv, 687—690).—The authors have found zinc in the human liver, in the liver and muscles of the ox, in eggs, and in wheat, barley, maize, and other vegetables. A human liver, weighing 1780 grams, yielded 2 centigrams of zinc oxide, and 913 grams of lean beef gave 3 centigrams of the oxide. Further researches are required before it can be affirmed that zinc is universally present in animal and vegetable bodies, but the facts here pointed out obviously possess a high importance in relation to toxicological investigations. R. R.

Acetic Acid, Formic Acid, &c., in Urine. By J. L. THUDICHUM (*Pflüger's Archiv. f. Physiologie*, xv, 12—26).—Urine having been evaporated to $\frac{1}{10}$th its bulk, is cooled and filtered, and the filtrate again evaporated, cooled, and filtered. The resulting liquid is evaporated to a syrup, cooled, filtered, made alkaline with calcined magnesia, and again filtered. This solution is mixed with concentrated sulphuric acid, filtered, diluted with water, and distilled until one-half has passed over.

The distillate is saturated with soda, evaporated on the water-bath until it becomes red, and then treated with ether. After separation of the ether, the solution is evaporated, acidified with sulphuric acid, and filtered from the benzoic acid thus separated. The filtrate is mixed with water and distilled. The distillate gives, principally, reactions for acetic and formic acids. The lead salts were prepared and purified by alcohol. Baryta salts were also prepared, which were found to contain a sulphur acid and nitric acid. F. J. L.

Thiocyanates in Urine. By J. L. W. THUDICHUM (*Pflüger's Archiv. f. Physiologie*, xv, 52—56).—The experiments of Gscheidlen (p. 205 of this volume), upon repetition, fail to prove the presence of thiocyanates in urine. The sulphurised body forms a lead compound insoluble in water, and does not volatilise when boiled with a large excess of phosphoric acid and evaporated to syrup; it cannot, therefore, be thiocyanic acid. The colour-reaction with ferric chloride upon which Gscheidlen's results depend, is manifested by other substances besides thiocyanic acid. F. J. L.

Contribution to the Knowledge of the Saccharifying Ferments. By J. SEEGEN and KRATSCHMER (*Pflüger's Archiv. f. Physiologie*, xiv, 593—605).—The authors endeavoured, by applying the method used by v. Wittich for obtaining the pancreatic ferment, to isolate the ferment of the liver. For livers containing much sugar, they found the method inapplicable, as sugar passes over in the glycerin-extract, and even when the latter was free from sugar, it soon gave, on dilution with water, a sugar-reaction, which could be accounted for only by the presence in it of both glycogen and ferment. The authors confirm the observation of Abeles that in a liver free from sugar, which has been boiled, formation of sugar occurs, on standing in contact with the air, and that, therefore, a saccharifying substance becomes active. Von Wittich and Lepine had already shown that in many animal tissues a saccharifying substance is present. The authors experimented with muscle, kidney, and brain; their experiments differed, however, from those of the above observers in the fact that the tissues were first *boiled*, then well washed and, the absence of sugar having been ascertained, were cut into small pieces and placed in a solution of glycogen. After some time, sugar always appeared, sometimes after only a few hours. The fact that the above organs had the one thing in common, that they were albuminous tissues, led the authors to experiment with chemically pure serum-albumin, egg-albumin, casein, and fibrin. These experiments showed that the diastatic action is connected with an albuminous body soluble in water.

The results of the authors' experiments may be summarised as follows:—

(1.) The albuminous tissues of the body, as well as all other albuminous bodies, which are soluble either partly or entirely in water, when in contact, for a longer or shorter time, with glycogen, possess the property of exerting a saccharifying action. By boiling the aqueous solution of the albuminous bodies, the diastatic action is momentarily arrested, but appears again after the space of two or three days. The minutest quantities of soluble albumin are sufficient to exert this sugar-forming action.

(2.) The action of these albuminous bodies on glycogen is qualitatively identical with that of saliva, and of pancreas-extract. There is, however, considerable difference both in the quantity and also in the rapidity of the action. The time required is longer, and the sugar formed by the action of albuminous bodies is much smaller in quantity than in the case of saliva or the pancreatic extract. The formation of sugar in a *boiled* liver is to be referred to the diastatic action of the albuminous tissue contained therein; whereas, in fresh *unboiled* liver, it is highly probable that, as in saliva and the pancreatic juice, a diastatic ferment is present in large quantities.

(3.) No method is known at present by which liver-ferment can be isolated. By all methods hitherto employed, glycogen is first extracted, and this contains, mixed with it, a diastatic element.

(4.) The authors' observations confirm the fact that in a pure solution of glycogen in glycerin, ferments are inactive. The formation of sugar occurs immediately when water is added to the mixture. E. C. B.

Experiments showing that the Poisonous Properties of Putrefied Blood arise from Organised Ferments. By V. FELTZ (*Compt. rend.*, lxxxiv, 953—955).—1 c.c. of putrefied blood, mixed with 5 c.c. of water injected into the veins of a rabbit, was found to kill it in 3 to 7 days.

After coagulation by exposure to a temperature of 80°, it was still full of bacteria, and proved fatal to a rabbit in 8 days. But when the putrefied serum was exposed to a temperature of 160° in a sealed tube for 4 hours, the blood became innocuous. There were then no living organisms visible under the microscope. W. R.

Chemistry of Vegetable Physiology and Agriculture.

Influence of the Leaves and Flowering Branches on the Nature and Quantity of the Sugar contained in the Flower-stem of the Agave. By M. BALLAND (*J. Pharm. Chim.* [4], xxv, 97—102).—Violette maintains that in the case of the beet the fall of the leaf causes a diminution in the sugar-production: he is supported by Duchartre and Boussingault, who mention the agave as another example: the author brings forward further experiments on the agave. The appearance and mode of growth of the agave are described: the production of a large quantity of sap, rich in sugar, is noticed during the flowering of the plant. The sugar in the expressed sap was determined by cupric solution both before and after inversion with hydrochloric acid, every precaution being taken to ensure that all the determinations were strictly comparable, and to ascertain that no substance in the juice interfered with the titration. From the tabulated experimental results, the author infers:—

1. That the saccharine matter is unequally distributed in the different parts of the agave: when the flower-stem is about to appear, most sugar is found in the great outer leaves; the ends of these leaves contain least sugar, and chiefly in the inverted form, not as saccharose. As the central parts are approached, the quantity of sugar diminishes; in the central placenta the two kinds of sugar are nearly equal in quantity.

2. The saccharine matter is also not uniformly distributed over the flower-stem: it is in greatest quantity at the bottom, and the top contains a larger proportion of saccharose. In plants not deprived of their leaves, the saccharine matter continually increases, the cane-sugar increasing whilst the reducing sugar remains almost uniform in quantity throughout. In plants whose leaves have been removed, the saccharine matter also increases, but is always in smaller proportion, and is almost entirely composed of inverted sugar. The removal of the leaves therefore exercises a direct influence on the saccharine matter contained in the flower-stem, the growth of which is slower after loss of the leaves, but is not completely arrested.

3. The development of the flowers exercises an exactly contrary effect. When it is arrested by cutting off the stem or mutilating the flowers, the proportion of cane-sugar increases, whilst the inverted sugar scarcely varies in quantity. The quantity of sap in the stem remains practically the same, its density increasing with the increase of the sugar.

Resuming, it is evident that not only the leaves but also the flowers exercise a marked effect on the formation of sugar in the flower-stem of the agave: probably the leaf is most active in the elaboration of sugar. F. C.

Action of Antiseptic and Toxic Vapours on the Fermentation of Fruits. By G. LECHARTIER and F. BELLAMY (*Compt. rend.*, lxxxiv, 1035). The authors made experiments on green apples weighing about 49 grams, these being placed in flasks containing severally carbolic acid, camphor, and a piece of potassium cyanide. As a means of comparison, one flask was also taken, containing the apple with atmospheric air only. This latter apple gave off, in 49 days, 404 c.c. of gas, and from that time till the end of the experiment, viz., 7 months, it remained completely inert. Under the influence of phenic and hydrocyanic acids, no gas was evolved in the course of 83 days, but in the case of the apple surrounded by camphor-vapour, 16 c.c. were given off. It would, therefore, appear that the action of camphor-vapour is less energetic, and diminishes without completely destroying the vitality of the cells. The authors have not continued these experiments, but M. Gayon has made some independent researches bearing out these results. J. M. T.

Action of Antiseptic and Toxic Vapours upon the Fermentation of Fruits. By M. W. GAYON (*Compt. rend.*, lxxxiv, 1036).—The author commenced a series of experiments in December, 1876, and March, 1877, upon apples, to determine the action of certain vapours upon the intercellular fermentation. The results obtained confirm the researches of M.M. Lechartier and Bellamy. The apples were suspended for observation in flasks containing small quantities of chloroform, ether, and carbon sulphide, whilst another was placed for comparison in atmospheric air. The flasks were fitted with tubes for taking off the gases. The fermentation and evolution of gas took place rapidly in the case of the apple suspended in air, in the first experiment 305 c.c. of gas being obtained in five weeks, whilst in the second 376 were obtained in 6 weeks. With chloroform and ether no gas was obtained, the apples merely changing colour, and having the appearance of being cooked. In the case of the carbon sulphide a commencement of fermentation took place, in one experiment 15, and in another 25 c.c. being obtained: the evolution of gas ceased and the colour changed as above in four or five days. From this it would appear that ether and chloroform act in the same way as phenic and hydrocyanic acids in the experiments of Lechartier and Bellamy, while the carbon sulphide seems to act in the same way as camphor.

J. M. T.

Analytical Chemistry.

Simple Suction Arrangement for Rapid Filtering. By C. HOLTHOF (*Zeitschr. Anal. Chem.*, xvi, 192—195).—The apparatus consists of a large flask, holding 5 or 6 litres, connected by caoutchouc tubing with another flask through a cork in which passes the funnel containing the filter. The large flask is connected also with a manometer, and with a short piece of glass tubing, which again passes through a cork into a tube shaped like a calcium chloride tube. To the end of the short glass tube within the calcium chloride tube is fitted a piece of caoutchouc tube, the other extremity of which is closed by a glass rod: a slit is made in this caoutchouc tube, which is thus transformed into a Bunsen valve. The narrow end of the calcium chloride tube passes downwards through a cork into the lower part of the cylinder of an air-pump, or into an ordinary large-sized zinc syringe. The syringe or air-pump cylinder communicates with the outer air by means of a short piece of glass tubing passing through a second hole in the cork; this glass tube is also closed by a Bunsen valve. When the piston of the syringe or cylinder is drawn back, the valve in the little piece of tubing closes and shuts off connection with the outer air, while that in the tube within the calcium chloride tube opens by reason of the increased pressure from within, and allows the air in the large flask to rush into the cylinder or syringe.

M. M. P. M.

A new Method of Analysing Carbon-compounds. By F. FRERICHS (*Deut. Chem. Ges. Ber.*, x, 26).—By this method the oxygen, nitrogen, hydrogen, and carbonic acid can be determined in one experiment, and perfect combustion ensured even in the most volatile bodies.

The substance to be analysed is heated in a glass tube, previously exhausted of air, with red oxide of mercury. The nitrogen and carbonic acid are determined by gas analysis, the water by means of a tube filled with phosphoric oxide. The quantities taken are such that the gases formed will not quite fill the tube, so that all danger on opening is avoided.

The substance, mixed with between 4—5 grams of accurately weighed mercuric oxide, is introduced into a tube 2 cm. by 50 cm., drawn out in the usual way. This tube is exhausted by means of a Sprengel pump, then sealed off, and placed, surrounded with magnesite, in an iron tube. A few hours' heating in an ordinary combustion furnace is sufficient. When cold the tube is again connected with the pump, the fine point broken off inside the connecting tubing, and the gases transferred to a eudiometer. When quite empty, the tube, still attached to the pump, is heated to redness, and the oxygen formed by the decomposition of the mercuric oxide is collected in another eudiometer. The gases are then measured in the usual way, and the amount of the oxygen contained in the substance calculated from the amount of oxygen in the eudiometer. The process of determining the water has not yet been carried out. C. L. F.

Estimation of Ammonia in the Air and Rain-water of Montsouris. By ALBERT LEVY (*Compt. rend.*, lxxxiv, 273—276).—The estimation of ammonia in the water was conducted in the following manner. To half a litre of filtered rain-water 1 c.c. of a 10 per cent. dilute sulphuric acid was added, and the whole evaporated in a capsule to 30 c.c. The residue was transferred to a retort, and the capsule rinsed out with 5 c.c. of the original water, which had been reserved for the purpose. Excess of potash was then added, and the liquid distilled: the ammonia was collected in standard acid, and the uncombined acid was afterwards estimated with standard alkali, with the aid of a few drops of tincture of cochineal.

In order to estimate the ammonia in air, the latter was slowly drawn by means of an aspirator through two bulbs containing water acidulated with 1 c.c. of dilute sulphuric acid of 10 per cent. The remainder of the operation was conducted in a manner similar to that which has been already described in the case of rain-water. The volume of air which passed through the apparatus was about 3·5 cubic metres.

Tables are given in the original communication showing the proportion of ammonia in the air and rain-water of Montsouris for every day in the months of November and December, 1876, and January, 1877.

The amount of ammonia in the air varied from 0·008 gram per cubic metre (minimum), to 0·066 gram (maximum). J. W.

Some Analytical Processes for Meteorological Purposes. Ammonia. By A. HOUZEAU (*Compt. rend.*, lxxxiv, 550—553).—The water is distilled, and the first portions, containing the ammonia, are collected. Some drops of a solution of litmus, prepared by adding to the blue solution just as much sulphuric acid as will turn it a wine-red colour, are added to the ammonia, and the amount is determined in the usual manner with standard acid. The accuracy of the process is much greater than is usually supposed. The results obtained by the author show that it is possible to estimate ammonia to 0·00001 of a gram. W. R.

Direct Determination of Soda in Potashes. By G. C. WITTSTEIN (*Dingl. polyt. J.*, ccxxiv, 85).—If the quantity of carbonic acid in a (supposed) mixture of sodium and potassium carbonates exceeds 31·8 per cent., or fall behind 41·47 per cent., it is evident that the substance is really a mixture of the two carbonates. If the former number represent the amount of carbonic acid, the substance consists of potassium carbonate only; if the latter number, of sodium carbonate only.

If the substance is proved, from a determination of carbonic acid, to be a mixture, it is only necessary to multiply the total weight of the two bases by 1·708763 (quotient obtained by dividing Na_2CO_3 by Na_2O), to deduct the result from the weight of mixed carbonates, and to divide the residue by 0·242663 (difference between 1·708763 and 1·4661; the latter number is obtained by dividing K_2CO_3 by K_2O) in order to obtain the amount of potash.

In order to obtain the amount of soda, the weight of the two bases is multiplied by 1·4661, the product is deducted from the weight of mixed carbonates, and the residue is divided by 0·242663.

M. M. P. M.

Detection of Alum in Flour. By J. C. BELL (*Analyst*, ii, 28). 50 grams of flour are mixed with 50 c.c. of water, 0·5 c.c. of logwood solution, and 5 c.c. of ammonium carbonate solution are added. The colour of the emulsion becomes lavender-blue, in place of pink, if $\frac{1}{10000}$th part of alum is present. M. M. P. M.

Estimation of Alum in Bread. By W. C. YOUNG (*Analyst*, ii, 13).—A slight modification of the "Normandy" process for the detection of alum in bread is recommended:—1,000 grains of bread are burnt down to a small bulk; the charred residue is treated with about 100 grain measures of hydrochloric acid, and warmed for a few minutes; about two ounces of water are then added, the whole boiled for five minutes, and filtered, &c. A solution containing about 250 grains of pure sodic hydrate is made in a very little water, and to this solution, when boiling, is very cautiously added the boiling acid solution of the charred bread, the whole boiled for a few minutes, filtered and washed. The filtrate, after the addition of a few drops of a concentrated solution of disodic phosphate, is slightly acidified with hydrochloric acid, and subsequently rendered just alkaline with ammonia and boiled. The precipitate is collected, washed, and weighed as aluminic phosphate. E. W. P.

Copper in Food. By A. DUPRÉ (*Analyst*, ii, 1).—Copper is found in almost all vegetables, as well as in animals, but rarely amounts to more than 1 grm. per 100,000. Copper added to green vegetables, as peas, &c., is injurious to the health, especially if the amount exceeds $\frac{1}{16}$ grm., and should therefore be looked upon as an adulteration. E. W. P.

Copper in Vegetables. By J. MUTER (*Analyst*, ii, 4)—It having been asserted that copper was necessary for the preservation of "tinned" vegetables, some such vegetables were examined, but copper was found only in those of a green colour. E. W. P.

Copper in Preserved Green Peas. By C. H. PIESSE (*Analyst*, ii, 27).—Copper was found in 9 samples of French preserved peas. The amount of copper varied from ·02 to ·20 parts per 1000. The copper was determined by precipitation as metal on a platinum dish forming the negative electrode of a small battery. M. M. P. M.

Estimation of Cobalt in Cobalt-Potassium Nitrite. By B. BRAUNER (*Zeitschr. Anal. Chem.*, xvi, 195—198).—The method depends upon the conversion of the double salt into cobalt silicate. The double nitrite is moistened with nitric acid, and washed into a platinum crucible containing a weighed quantity—about five times the weight of the nitrite—of finely powdered quartz, or glass, preferably the former. The mixture is dried, fused, and weighed. The increase in weight of the quartz-powder is multiplied by 0·2726, and the quotient gives the amount of metallic cobalt. If nickel be present, the two metals may be precipitated as hydrates by addition of caustic potash, reduced in hydrogen, and weighed, the amount of nickel being determined by difference. M. M. P. M.

Analysis of Chrome Iron Ore. By A. CHRISTOMANOS (*Deut. Chem. Ges. Ber.*, x, 10—20).—It is not possible to oxidise native chromite in the fiercest oxyhydrogen flame; but the addition of even small quantities of an alkali, lime, or magnesia, renders it easy to attack.

The author has, in the course of a number of analyses of chromites from various sources, had occasion to try all methods of estimation in present use, but has found none of them perfectly satisfactory.

The method selected by him as the most trustworthy, was that of Peligot and Clouet, which he has brought to a state of extreme accuracy, and by it executed a complete determination in one day. Pure chromite, the actual mineral, consists of chromic oxide and ferrous oxide, in the proportions of the magnetic oxides (R_3O_4 or $RO + R_2O_3$); all other constituents are contained in the matrix.

As the latter often encloses the crystals of chromite, or just as often is enclosed in them, the discrepancies in the analyses published at various times can easily be accounted for.

Very often silicates and oxides of calcium and iron are found, in addition to the ordinary matrix of magnesium silicates and magnesium aluminium silicates. These varieties must be carefully distinguished from those in which the magnesium and aluminium oxides have taken the place of part of the chromium and iron in the actual mineral.

The essential feature in the analytical operation is the reduction of the chromite to an absolutely impalpable powder. This is greatly expedited by calcining thoroughly powdered ore and continual sifting through muslin. As the pure chromite, obtained by long powdering, sifting and levigation, contained very decidedly less magnesia and alumina, it may be accepted as a fact, that the amounts of those bodies usually given as constituents, are really only accessories of the mineral.

Of this finely powdered ore, from ·3 to ·5 grm. is intimately mixed in a platinum crucible with ten times its weight of pure calcined silica and magnesium carbonate, and exposed to a very high heat for two hours. The fused mass is allowed to cool, and exhausted with hot water with the usual precautions. The normal colour of the fused mass is pure yellow, but often it will be green or brown. This is due not to manganese, but to the coloration effected by red sodium ferrate and blue perchromate, which are formed at a high temperature. After boiling the solution for a few minutes, the colour is changed to a dark yellow, while black iron oxide is precipitated, which changes ultimately to the ferric hydrate. The boiling must not be checked till the above reaction is complete, as otherwise the iron would be precipitated with the alumina, and detract from its subsequent purity. When the reaction is complete, the supernatant liquid is partly decanted, partly filtered from the precipitated magnesium silicate and ferric hydrate. The filter should be as small as possible, and the liquid brought, as concentrated as possible, into a large, thin flask.

The precipitate on the filter is thoroughly washed, sucked dry, and introduced into a porcelain dish. The filter-paper is dried, and incinerated in the usual way over the dish, and the ash placed in it. The platinum crucible in which the original fusion was made, and which has been standing with concentrated hydrochloric acid, is heated, and its contents are poured into the porcelain dish, with a few drops of nitric acid. The liquid in the dish is now evaporated to dryness, and the residual yellow powder, instead of being heated on the sand-bath, is moistened with strong hydrochloric acid and again evaporated.

The silica is then separated, filtered, dried, and weighed in the usual way; and the iron is precipitated from the filtrate and weighed as ferric oxide. The filtrate is now freed from lime, if any, in the usual way, and from the last filtrate the magnesia is precipitated.

The determination of the alumina and chromic acid contained in the yellow filtrate in the thin glass flask proceeds simultaneously with the above.

The alumina is present as sodium aluminate, while the chromium oxide has been converted into sodium monochromate.

The filtrate is acidified to slightly above neutralisation with sulphuric acid, so that the alumina precipitated at first redissolves. The flask is now heated to boiling, ammonia added in slight excess till the bichromate is converted into the chromate, the ammonia expelled by boiling, and the precipitated alumina washed by repeated boiling and decantation till perfectly white. It is then determined in the usual way as Al_2O_3.

The filtrate now containing nothing but the chromium, is treated with a large amount of equal bulk of strong sulphuric acid and alcohol, and heated to boiling, till hydrochloric acid fumes are evolved. Cold water is then added largely, and caustic ammonia in slight excess, by which the chromium hydrate is precipitated: the ammonia is expelled by boiling, care being taken to maintain the water at the same level. The chromium oxide is then ignited in a closed platinum crucible at white heat, thus converting the hydrated oxide into the sesquioxide.

Chromites containing titanium are very rare. Chrome ochre, which is now and then found as a green scale on pure chromite crystals, must be dissolved off with hydrochloric acid, and estimated by itself.

The estimation of the chromium oxide alone for technical purposes can be effected far more rapidly. About ·3 grm. of finely powdered chromite is intimately mixed with $\frac{1}{3}$ of a mixture of from 6—10 grms. of perfectly dry and finely powdered caustic soda, and 10—15 grms. of magnesia. The mixture is introduced into a large platinum crucible, and washed out from the mortar with small portions of the same mixture, the rest of which is finally added to the contents of the crucible. The mixture is then heated in the covered crucible, stirring now and then with a thick platinum wire.

The fused mass is extracted by prolonged boiling with water, and the solution is filtered. By this means the whole of the aluminium and chromium are obtained in the filtrate, with inconsiderable amounts of lime and magnesia.

This filtrate may be titrated directly if the chromium is to be determined volumetrically. If, however, it is desired to precipitate the chromium oxide, the solution, acidulated to slight excess with hydrochloric acid, must be treated with ammonia in excess, and ammonium carbonate and oxalate, and subsequently boiled till all smell of ammonia vanishes, keeping the water at the same level. The best solution for titration is one of ammonio-ferrous sulphate, in the proportion of 23·52 grm. in $\frac{1}{4}$ litre of water, in which according to the formula—

$$2CrO_3 + 6FeSO_4 + 3H_2SO_4 = Cr_2O_3 + 3Fe_23SO_4 + 3H_2$$

1 c.c. = ·006096 grm. of chromium oxide.

On addition of such a solution to the chromic filtrate, the bichromate yellow gradually changes through brown to green, the moment of completion being shown by the sudden change of colour to dark emerald-green, due to the sudden conversion of the chromic acid to the oxide or chloride at the expense of the ferrous salt.

With the greatest precaution, however, this method can never be brought to the requisite state of accuracy, as the change is by no means distinct, even to a practised eye. The author has tried the following modification with extremely accurate results. The chromium solution is mixed in excess with a known amount of the ferrous salt solution, and the excess of ferrous oxide determined by permanganate of potash. The details of experiment do not differ materially from the known method; the amount of ferrous solution added should be calculated in excess of the amount that would be required by an ore containing as much as 70 per cent. of chromium oxide. The violet colour of the permanganate is distinctly visible through the green of the chromium chloride.

The author gives several modifications, which do not differ essentially from the above, except that in one method, the chromium solution with the excess of standard iron solution added, is placed in a burette, and from this, dropped into a mixture of 10 c.c. permanganate solution, water and sulphuric acid. The whole volume and the amount used for titration being measured, the amount of superfluous ferrous salt can be easily calculated, and therefrom the quantity requisite for titration of the chromium salt. This number multiplied by 0·45357, gives the weight in grams of chromium oxide.

The results are accurate. C. L. F.

Analysis of Chrome Ores. By J. FELS (*Dingl. polyt. J.*, ccxxiv, 86—92).—The author has experimentally examined the various processes in general use. He gives the preference for rapidity, ease of execution, and exactness, to the methods of Calvert: fusion with soda lime and sodium nitrate; Britton: fusion with soda lime and potassium chlorate; and Dittmar: fusion with a mixture of borax and alkaline carbonates. M. M. P. M.

Separation of Manganese in the form of Anhydrous Sulphide. By A. CLASSEN (*Zeits. Anal. Chem.*, xvi, 319—320).—The precipitation of manganese as anhydrous (green) sulphide presents many advantages, as the precipitate (unlike the flesh-coloured hydrated sulphide) quickly settles down and is easy to filter and wash. Fresenius finds that the conversion of the flesh-coloured into the green sulphide is especially quick when the solution is at once mixed with an excess of ammonium sulphide. The presence of ammonium chloride, however, which it is necessary to add, hinders or even prevents altogether the conversion of the flesh-coloured into the green sulphide; consequently this method cannot be employed. The separation of the manganese as anhydrous sulphide may, however, be effected with certainty by first heating the solution with calcium oxalate, then adding ammonia and sulphide of ammonium. The green sulphide is then at once formed or a mixture of the two. The complete conversion takes place after warming on a sand-bath. Oxalic acid and oxalate of ammonium behave similarly to oxalate of lime, the latter, however, is to be preferred. The presence of ammonium chloride does not influence the formation of the green precipitate. D. B.

Estimation of Sugars, and Acid in 37 varieties of Eating Apples and six varieties of Cyder Apples. By A. TRUELLE (*Bull. Soc. Chim.* [2], xxvii, 398—405).—This investigation was undertaken to test the correctness of Buignet's theory, that no relation can be established between the proportion of sugars in these fruits and their acidity. The extract of the fruit, after being freed from colouring matter by basic lead acetate, was titrated with baryta-water, with litmus-paper as indicator for acid, and with Fehling's solution for sugars. A very great difference is noticeable in the amount of sugar; the largest quantity of reducing sugar being 13·386 per cent. of the pulp, and of non-reducing sugar 5·6 per cent. The greatest amount of total sugar was 14·44 per cent., and the greatest amount of acid calculated as H_2SO_4, 2·274 per cent. No relation was observable between the proportion of the two sorts of sugar and the acid. W. R.

Creasote and Carbolic Acid. By ADOLPH GRÄTZEL (*Arch. Pharm.* [3], x, 130—137).—The author compares the behaviour to different reagents of Marson's English wood-tar creasote carbolic acid and beechwood-tar creasote. To 15 c.c. of the aqueous solution of each of these bodies one drop of the different reagents was added.

	Beech-wood Tar Creasote.	Carbolic Acid.	English Creasote.
Ferric chloride (1 in 10)	Blue coloration, turning first brown, and then orange.	Permanent violet coloration.	Blue coloration, turning olive-green, and then dirty yellow
Ferric acetate (1 in 10)	Brown coloration, with a violet tinge. Finally, a brown precipitate.	Clear brown colour	Clear brown colour.
Ferric sulphate (1 in 20)	Blue, with a tinge of violet, and lastly a brown precipitate.	Permanent violet coloration.	Grass-green colour, and lastly, a yellow precipitate.
Lead nitrate (1 in 10).	No change........	Cloudy, and lastly slight precipitate.	Like carbolic acid.
Zinc chloride (1 in 10)	White precipitate, soluble in excess.	Slight precipitate, insoluble in excess	Like carbolic acid.
Lead acetate (1 in 10).	White precipitate, soluble in excess.	Slight precipitate, insoluble in excess.	White precipitate, partly soluble in excess.

Next when these bodies were dissolved in ten times their weight of alcohol, their reactions were—

Aqueous ferric chloride (1 in 10)	Blue coloration, turning green.	Violet coloration, turning green.	Green coloration, turning a fine blue.

When the concentrated substances were taken, the reactions were—

Alcoholic ferric chloride	Dirty violet.......	Yellow-green, turning brown.	Green, turning brown.

Pure guaicol and creasol behaved in the same manner as beechwood-tar creasote. E. N.

Prussic Acid from Cassava. By E. FRANCIS (*Analyst.* ii, 4).—Bitter cassava being poisonous, whereas sweet cassava is harmless, it was supposed that the latter would not contain hydrocyanic acid, whereas the former was known to contain it. On examination it was found that this acid was present in both; in the sweet cassava to the amount of ·0168 per cent. (average), and in the bitter to the amount of ·0275 per cent. The method of analysis was as follows:—500 grams of the root were quickly grated into 500 c.c. of water, the mixture allowed to stand to allow of deposition of the starch (30 per cent.), then squeezed through linen and distilled into water made alkaline with soda. The acid thus obtained was determined volumetrically and gravimetrically. Hydrocyanic acid is given off spontaneously by the roots when grated. The roots of the sweet cassava contain 59·4 per cent. water, and those of the bitter, 61·35 per cent. E. W. P.

Extraction and Estimation of Piperine in Pepper. By CAZENEUVE and CAILLOL (*Bull. Soc. Chim.* [2] xxvii, 290).—The authors have applied the chalk process with great success to the extraction and estimation of various alkaloïds. They therefore tried it in the extraction and estimation of piperine in pepper in the following way:—Ground pepper is treated with twice its weight of slaked lime and a sufficient quantity of water, the whole being heated to boiling for a quarter of an hour. The piperine is in no way altered by this treatment. The solution is then evaporated to dryness on the water-bath, and the powder exhausted in a suitable apparatus with commercial ether, from which the piperine can be obtained nearly pure on evaporation. Piperine forms large crystals of a faint straw-yellow colour.

To obtain it perfectly pure, it must be dissolved in alcohol and recrystallised. The crystals obtained from the ether are, however, quite pure enough to weigh, and thence determine the amount of alkaloïd in the pepper. The authors operated on 10 grams of pepper. The piperine from the ether solution is dried at 100° and weighed:

Sumatra pepper	gave	8·1	per cent.	piperine.
Black Singapore do.	„	7·15	„	„
White do. do.	„	9·15	„	„
Penang do. do.	„	5·24	„	„

The superior richness of the white Singapore pepper in piperine is due to the absence of the inactive pericarp in that variety.

C. L. F.

Toxicological Detection of Colchicine. By E. DANNENBERG (*Arch. Pharm.* [3], x, 97—116).—In employing the Otto-Stas process for detecting alkaloïds, it is better to employ chloroform or amyl alcohol instead of ether to separate the colchicine, these reagents being more energetic in their action and capable of dealing with smaller quantities of the alkaloïd. The best reagent for detecting the presence of colchicine is nitric acid, employed according to either Flückiger's or Erdmann's methods, as they give a clear rose colour where all the other tests fail. The former of these is, however, to be preferred. Numerous test experiments were made to ascertain the relative delicacy of the different reagents. Fifty grams of meat were digested with 100 grams of water for two days at a temperature between 30° and 40°, and the solution thus obtained mixed with small quantities of colchicine. When as usual ether was employed to separate the alkaloïd, the ordinary tests became uncertain when the amount of colchicine was only 1 in 17,000. The reaction with nitric acid was, however, distinct when the amount of alkaloïd was only one-fourth as great. When, however, ether was replaced by amyl alcohol or chloroform, the usual reagents remained available until the colchicine was reduced to 1 in 60,000, and the nitric acid reaction, according to Flückiger's method, until it was only 1 in 220,000. E. N.

Micro-chemistry as applied to the Identification of Tea-leaves, and a New Method for the Estimation of Theine. By A. WYNTER BLYTH (*Analyst*, ii, 39—42).—The leaf is boiled with a little water on a watch-glass, an equal bulk of calcined magnesia is added, and the whole is evaporated to the size of a large drop. This drop is placed on a thin circular disc of glass on which rests a somewhat thick ring of glass; the glass disc is heated on an iron plate carrying a cup of mercury with a thermometer-bulb immersed therein, until dry; another thin glass disc is placed on the top of the ring; and the temperature of the plate is raised to about 200°. If a sublimate be formed, the upper disc is made to form the lower portion of a new "subliming cell," and the sublimation is repeated at a temperature of 110°. If the sublimate is volatile at this temperature it is almost certainly theine. A microscopic examination may be made. The smallest fragment of a leaf is sufficient for the detection of theine. If no sublimate is formed at 200° to 220° the leaf is not that of the tea, or other theine-yielding plant.

Theine may be determined by boiling from 1 to 2 grams of tea or coffee with 70 c.c. of water for an hour in a flask fitted with an upright condenser; transferring the decoction and residue to a basin; adding from 1 to 2 grams of magnesia—according to the weight of tea or coffee used; evaporating nearly to dryness; transferring the residue to an iron plate; covering it with a tared glass funnel, the edges of which are well ground; heating to 110° for some time, and, finally, to 200° or 220°. So soon as the funnel ceases to increase in weight, the sublimation may be stopped. The increase in weight represents theine.

Tea-leaves always contain manganese. M. M. P. M.

Investigations on Food. By E. REICHARDT (*Arch. Pharm.* [3], x, 339—364).—*Butter adulterated with Lard.*—Good fresh butter possesses the well known agreeable taste, and a slight smell of milk, while rancid butter smells very disagreeably. The latter may be converted into an eatable food by treatment with water, in which case the soluble rancid parts are removed. The taste of butter varies, however, according to the fodder used. The colour of pure butter is yellowish-white to reddish-yellow, and again depends upon the class of animals as well as the fodder used. Its colour is often adulterated by means of small quantities of beetroots or other plants possessing colouring power. The colouring matter may be detected by treating the butter with strong alcohol. Salt is added to the butter in order to increase its durability. In eight different qualities of pure butter 0·57 to 6·00 p.c. chloride of sodium was found. The determination of salt is made by treating the butter with 3—4 pts. of water at 100°, and filtering the aqueous extract. The chlorine can then be determined in the filtrate, or the latter may be evaporated. Chalk, gypsum, oxide of zinc, starch, &c., form solid additions to butter. The quantity of casein in butter is very small (·2—·5 p. c.). The best kinds of butter contained 1·25 to 9·0 p. c. of water. Pure butter contains 90·0 to 98·0 p. c. of butter-fat, varying with the amount of water. Butter used for cooking purposes was found to contain from 50—90 p. c. The following table gives the various fats existing in butter, with their relative specific gravities, their melting and solidifying points :—

Fat.	Sp. gr.	Melt. pt.	Cryst. pt.	Fatty acid.
Olein......	0·914	liquid	+9—10° (?)	$C_{18}H_{34}O_2$
Butter-fat..	1·056 (?)	?	0° (?)	$C_4H_8O_2$
Caproin....	?	?	?	$C_6H_{12}O_2$
Caprin	?	?	?	$C_{10}H_{20}O_2$
Laurostearin	?	44—48°	44—45°	$C_{12}H_{24}O_2$
Myristin ..	?	31 (46°)	?	$C_{14}H_{28}O_2$
Palmitin ..	?	61° ?	46° (?)	$C_{16}H_{32}O_2$
Stearin	?	62°	?	$C_{18}H_{36}O_2$

	Sp. gr.	Melt. pt.	Cryst. pt.
Oleic acid	0·898	14°	4°
Butyric acid	0·967	liquid	
Caproic acid	0·931	—	
Capric acid............	0·910	27—46	30°
Laurosteric acid	0·883	44°	?
Myristic acid..........	?	54° (49°)	?
Palmitic acid	?	62°	55° (?)
Stearic acid	?	69°	?

Beef fat melts at 39° and solidifies at 37°.

Mutton fat melts at 50° and solidifies at 37°, often at 39·41°.

Deer fat consists of two kinds, a substance soluble in hot alcohol and an insoluble one. The insoluble portion has a specific gravity of 0·968°, melts at 49·5°, and crystallises at 46·5°. The portion soluble in boiling alcohol crystallises on cooling the alcoholic solution, while an oily fat remains in solution. The melting point of this portion is 57°, and its density 0·970°.

Hog's lard has a specific gravity of 0·938 at 15°, and melts at 40·5°.

The melting point of cow's butter is 33—37°, while that of artificial butter is 27—31·7°. The composition of the former was found to be 75·63 p. c. C., 11·87 H., and 12·50 O. The butter was dried at 110° and filtered. The melting point of butter is determined in the usual manner by placing the sample in a small glass tube, the end of which is drawn out to a fine point, and observing the melting of the butter by a thermometer placed on the side of the tube. The sample must be perfectly free from water and salt.

The most satisfactory way of detecting adulteration of butter with fat is its behaviour to various solvents. Horsley's method consists in purifying the butter by remelting it in water, washing, and testing it with ether at 18·5°. Pure butter is said to dissolve in the ether, forming a clear lemon-yellow liquid, while hog's lard, beef fat, mutton fat, and tallow form turbid milky solutions. Balard improved this method by using 1—2 grams of butter, treating the latter in the above manner, and weighing the residue.

The fat of pure butter boiled with concentrated potash or soda-lye saponifies quickly and regularly, and the soap when taken up with water, separated by salt, and washed, is not so firm as in the case of adulterated butter. D. B.

Butter-fat, its Analysis and Composition. By E. W. T. Jones (*Analyst*, ii, 19—25).—The author recommends that the sp. gr. be taken immediately after melting and filtering the fat; his experiments show that the sp. gr. of butter-fat increases when the fat is maintained at a tolerably high temperature for some time. He does not, however, place great reliance upon the sp. gr. as a test for the purity of butter-fat. The process for estimating soluble and insoluble fatty acids is essentially the same as that of Muter (this *Journal*, vol. i, 1877, p. 233). Saponification is carried out by the use of an approximately semi-normal alcoholic potash solution, at a temperature of 50° or so, and is followed by decomposition of the soap with semi-normal sulphuric acid. The excess of acid is determined by deci-normal soda. The exact relation between potash and acid solution must be ascertained.

The author recommends to run into a beaker an amount of potash and of acid equal to that used for saponification and decomposition, and to determine the excess of acid by deci-normal soda simultaneously with the actual butter analysis.

The insoluble fatty acids should be dried at a temperature somewhat below 100°.

In an addendum to his paper (*Analyst*, ii, 37—39) the author details a few experiments, which show that repeated washing of the insoluble acids with hot water considerably reduces the percentage amount of these acids, but does not very much increase the amount of soluble acids, if these are calculated as butyric acid. M. M. P. M.

On a New Method of Analysis of Milk, and on a New Carbohydrate in Milk. By H. Ritthausen (*J. pr. Chem.* [2], xv, 329—349).—A solution of copper acetate, or, better, one of copper sulphate, because of the more rapid subsidence of the precipitate, is employed to precipitate the casein, the strength recommended being 63·5 grams crystallised pure copper salt dissolved in 1 litre of water, 10 c.c. of which correspond to 0·2 gram CuO. A solution of potash or soda, 10 c.c. of which is equivalent to 10 c.c. of the copper solution, is also required, and is added to prevent the formation of basic copper salts; but as milk contains free alkali and triphosphates, it is found that only seven-tenths of the calculated amount of the alkali is required for the complete decomposition of the copper salt.

The solution in which the precipitate is produced must not be alkaline, but neutral, or only slightly acid, otherwise the casein-copper precipitate is dissolved by the alkali, forming a blue liquid. In the analysis 10—20 c.c. of milk, which should be weighed and diluted to at least twenty times its volume, is employed, and to it is added about 5 c.c. of copper sulphate solution. The precipitate thus formed is filtered off on a tared filter and washed with water; in the filtrate and washings the milk-sugar is determined by Fehling's method. The copper compound contains further the protein matter in combination with copper, together with the whole amount of fat contained in the milk. The fat is removed by repeated washings with ether, and finally with alcohol, and determined. The residue, after drying over sulphuric acid, should be of a light blue colour, and powdery. If all the fat is not removed, the residue, instead of being powdery, is of a dark blue colour, and glassy. This residue is then weighed, dried at 125° for 1—2 hours until its weight remains constant, and finally cautiously ignited, the loss corresponding with the amount of albuminoïd substances present in the milk; but the amount of copper in combination is always above that necessary to combine with the casein, &c., a portion always remaining combined as phosphate. For this no constant has as yet been determined, whereby correction may be made. A certain amount of carbon is also found in the ignited copper oxide, and this also must be determined. Water is determined by heating to 105° 2—3 c.c. of milk with 10—15 grams of ignited sand, and the ash is determined by difference, the other constituents being already known. The amount of nitrogen present in milk appears to be about 15·5 per cent. On evaporating the solution which contains the fats, a portion is found to be less soluble in ether, and to solidify as an opaque brown mass, being soluble in water, and reducing copper solutions to the suboxide, but not reducing a mixture of bismuth nitrate and potash. Alcohol added to the aqueous solutions of this substance causes a precipitate which will not crystallise from water. It is, therefore, not identical with milk-sugar, but owing to the small amount of material no further investigations could be made. E. W. P.

Mare's Milk. By J. Muter (*Analyst*, ii, 42).—The following numbers represent the mean of a series of analyses of genuine mare's milk:—

Fat	0·50	per cent.
Sugar	6·74	„
Casein, &c.	1·67	„
Ash	0·41	„
	9·32	„

One sample, exceptionally rich in fat, yielded the following numbers:—

Fat	1·70	per cent.
Sugar	6·11	„
Casein, &c.	2·92	„
Ash	0·50	„
	11·23	„

The foal of the mare yielding this milk was constantly sick; by regulating the diet of the mare, the milk was reduced to its normal condition, and the foal ceased to exhibit symptoms of sickness.

M. M. P. M.

The Peptones of Beer Worts. By V. GRIESSMAYER (*Deut. Chem. Ges. Ber.*, x, 617—622).—Gorup-Besanez has shown that by means of the biuret reaction the peptones may be distinguished from the parapeptones and albuminoïds. A series of experiments has led the author to the conclusion that wort and beer contain peptones and parapeptones, but that these bodies cannot be distinguished by the above reaction, which is of a doubtful value. C. S.

Optical Behaviour of Wines, &c. By C. NEUBAUER (*Zeits. Anal. Chem.*, xvi, 201—216).—The author now recommends complete decolorisation of all red wines before testing in the polaristrobometer (see this *Journal*, 1876, ii, 666). Animal charcoal is used: it is sometimes necessary to precipitate with lead acetate before using the charcoal. A number of experiments with grape wort, mixed during fermentation with cane and grape sugars, are detailed. In every case the wine, after complete fermentation, showed considerable dextrorotatory action when grape sugar was employed, but lævo-rotatory action when raw sugar was used.

A new instrument for optically examining wine is described, but it cannot be properly understood without the woodcut.

M. M. P. M.

Wines coloured by Fuchsine. By S. COTTON (*Bull. Soc. Chim.* [2], xxvii, 154—155).—When other methods fail to reveal the presence of fuchsine in wines, the author uses the following:—The wine is filtered, and the filter is put back into the bottle and treated with ether, ammonia, and acetic acid, in the usual manner. He also converts the fuchsine into aniline yellow, by treating it with nitric acid at a moderate heat, and adding ammonia to the product of evaporation; a yellow coloration is produced, and on addition of potassium cyanide, the colour changes to reddish-purple. W. R.

Technical Chemistry.

Industrial Preparation of Pure Salts of Alumina. By DUCLA (*Compt. rend.*, lxxxiv, 949—951).—The usual impurity in ordinary sulphate of alumina is iron, and for this reason it is rejected by printers. The following process yields pure alumina, even although impure clay is used in its manufacture.

Ordinary commercial sulphate is treated with a mixture of carbonate and milk of lime, obtained by a process to be afterwards described. A mixture of calcium sulphate and hydrates of iron and alumina are produced. The mixture is digested with caustic soda to dissolve the alumina, and the sodium aluminate is decomposed by the carbonic acid evolved by treating the aluminium sulphate with the mixture of milk of lime and carbonate. The precipitated alumina may be dissolved in any requisite acid; it is free from iron. The sodium carbonate is treated with lime, caustic soda being regenerated, and the mixture of calcium carbonate and caustic lime for addition to the aluminium sulphate is thus obtained. If desired, the calcium sulphate may be mixed with ammonium carbonate, giving ammonium sulphate and calcium carbonate. W. R.

Preparation, and Use in Casting Steel, of Alloys of Silicon and Manganese. By SERGIUS KERN (*Chem. News*, xxxv, 226—227).—In order to prevent the formation of blowholes in ingots of steel, Bessemer uses silicide of iron, the silicon acting chemically on the carbonic oxide, which gives rise to these defects, by the following reaction:—$2CO + Si = SiO_2 + 2C$. The resulting ingots proved, moreover, to give steel with a very high degree of tension. The free carbon acts very energetically on the oxides of iron, and gives the following results:—$Fe_2O_3 + 3C = 3CO + Fe_2$, or $2FeO + 2C = 2CO + Fe_2$. The author prefers to use an alloy of silicon, manganese, and iron in order to reduce at the same time the iron oxides of the metallic bath by the manganese of the alloy, and to prevent the formation of blowholes in the ingots by means of the silicon of the alloy. 1 to 1¼ p. c. of an alloy with 70 to 75 p. c. of Mn, 18 to 16 p. c. of Fe, 10 to 6·50 p. c. Si, and 2 to 2·50 p. c. C is added at the end of the operation in melting steel in Siemens-Martin furnaces. The results of the use of this alloy are highly favourable.

The following process is further recommended for the production of silicon alloys with ferro-manganese. The raw mass consists of:—

Ferro-manganese (60 to 70 p. c. Mn, 6 to 7 p. c. C)....	220	pounds.
Iron in small strips	25	„
Quartz of good quality	100	„
Calcium fluoride....................................	155	„
	500	„

All these substances are mixed with the iron in strips, and with coal-tar in such a quantity as to obtain a pasty mass, which is well dried and divided in four parts, and placed in four crucibles, which are 1¼ to 1⅓ of an inch in thickness. They are placed in coke furnaces for about five hours, after which the resulting alloy contains 6·650 p. c. Si, and 1 to 1·5 p. c. C. Alloys with 7 to 12 p. c. Si may be obtained by using ferro-manganese with a higher percentage of carbon, and by increasing the above quantities of quartz and CaF_2. Calcium fluoride gives with quartz the following products:—$12CaF_2 + 4SiO_2 = 4CaSiF_6 + 8CaO$. The $CaSiF_6$ next very easily gives silicon to the melting ferro-manganese alloy, the resulting oxide of calcium forming with the remaining quantity of quartz and a certain quantity of manganese, a liquid slag, which protects the liquid metal from further oxidation. This process gives silicon-manganese alloys with less expense than by melting ferro-manganese with quartz alone. D. B.

Metals accompanying Iron. By A. TERREIL (*Chem. News*, xxxv, 226).—The numerous analyses made during several years of the principal ores of iron and of the metallurgic products, have convinced the author that iron, like platinum, is almost always accompanied in its ores by several metals, which are found in the metallurgic products of this metal. These metals are manganese, nickel, cobalt, and chromium, principally magnetic metals, whose presence has been considered as characteristic of meteoric irons, and also copper, vanadium, titanium, and tungsten, whose presence is accidental. The author uses the following method to detect these metals. After having treated the substance in the ordinary way, either with aqua regia, or by hydrochloric acid and chlorate of potash, the solution is filtered and washed with distilled water. The filtrate is then poured gradually, with stirring, into ammonia, and the precipitate thrown on a filter, and washed with distilled water. The metals are at this point of the analysis divided into the following groups:—1. Metals found in the residue insoluble in acids: *titanium* and *tungsten*. 2. Metals precipitated along with the oxide of iron: *chromium* and *vanadium*. 3. Metals dissolved in the ammoniacal liquor: *copper*, *nickel*, *cobalt*, and *manganese*. From the residue the tungstic acid may be dissolved out by ammonia, and the titanic acid by concentrated and boiling sulphuric acid. The presence of titanium is indicated by the violet coloration of the liquid on the addition of zinc, while that of tungsten is shown by the greenish-yellow powder, easily characterised by the blowpipe. When there is too little titanic acid in solution, it is of course best to evaporate to dryness, and examine with the blowpipe. The chromium and vanadium are detected by suspending the precipitate of oxide of iron in a solution of pure potash, heated up to 90°. Permanganate of potassium is then added, as long as the latter is decolorised. The permanganate transforms chromium and vanadium into chromate and vanadate of potassium. The solution, after complete transformation (when it assumes a green colour), is filtered, the alkaline liquor saturated with acetic acid and filtered; and to a portion of the filtrate are added a few drops of acetate of lead. Chromate of lead is thereby produced, which may be mixed with vanadate. Vanadium is detected in the other portion of the liquor by adding a solution of tannin recently prepared. The vanadic acid then slowly forms with the tannin a blue-black precipitate, although the liquid is immediately coloured. When the yellow precipitate of lead chromate contains vanadate of lead, it is likewise coloured black-blue, or greenish-black, when it is moistened with the solution of tannin. The metals of the last group are detected by adding to the ammoniacal liquor a few pieces of pure potash, which throws down the metals as oxide. The precipitate is collected on a filter, washed, and a small portion of it tested for manganese by nitre and potash. The copper is separated from the hydrochloric acid solution of the precipitate by sulphuretted hydrogen, and the filtrate, after boiling and concentrating, is treated with ammonia, which shows the presence of nickel by its assuming the blue-violet tint. The cobalt is detected in the following manner:—The ammoniacal solution is treated with a few drops of permanganate of potassium, which peroxidises the cobalt and precipitates the manganese. The mixture is filtered, supersaturated with hydrochloric acid, and left at rest for 24 hours, after addition of a little alcohol. A violet-rose precipitate of roseo-cobaltic hydrochloride will be obtained if cobalt be present. In conclusion, the author states that the proportions of metals accompanying iron are ordinarily very slight in the metallurgic products, whilst in the native or meteoric irons these proportions often reach 10 per cent. D. B.

Silk Industry. (*Dingl. polyt. J.*, ccxxiv, 99).—A paper of purely technical interest, giving an account of the chief processes in the manufacture, and especially in the dyeing of silk. M. M. P. M.

Paris Sewage. By Ch. Lauth (*Compt. rend.*, lxxxiv, 617—620).—Two vessels, one containing ordinary sewage, the other sewage saturated with air, were placed aside, to watch the effect. The former soon became black and offensive, whilst the second, after two months, was still inodorous.

The chemical action of the aëration was as follows:—

	Insol N.	Sol. N.	N. as nitric acid.	N. as ammonia.	Total N. by volume.
Before aëration..	14·70	20·65	1·176	8·4	38
After " ..	8·05	26·95	1·122	14·0	38

The effect of lime on sewage was next tried; it remained inodorous and colourless after two months, and gave on analysis the following results:—

	Insol. N.	Sol. N.	Nitric acid.	Ammonia.
Without treatment	14·70	20·65	1·17	8·4
Treated with lime............	10·15	25·55	2·60	18·20
Treated with lime and aërated.	6·65	28·87	2·12	21·35

These results show that the development of putrefaction producing sulphuretted hydrogen may be avoided, not only by treating sewage with lime, but by mere aëration. F. J. L.

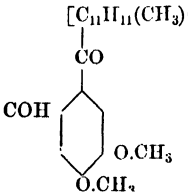
PAPERS READ BEFORE THE CHEMICAL SOCIETY.

No. XXIV.—*On Narcotine, Cotarnine, and Hydrocotarnine.* Part V. *On New Cotarnine Derivatives and on Nor-opianic Acid.*

By C. R. Alder Wright, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School.

§ 1. *Various Experiments with Cotarnine.*

The results detailed in the previous portions of these researches having led to the development of the alternative partially-dissected formulæ for narcotine—



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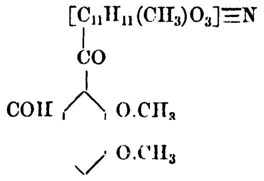


of which the former is rather the more probable, it appears to be desirable that further information should be gained as to the character of the further dissections appropriate to the radical $C_{11}H_{11}(CH_3)O_3$. With this object in view, a number of fruitless experiments have been made with both cotarnine and hydrocotarnine: no definite substances could be isolated from the products of the action on these bases of various oxidising agents, *e.g.*, chromic acid, permanganate, nitric acid, &c.; it was not found practicable to reproduce the conditions under which the "cotarnic acid," $C_{11}H_{12}O_5$ of Matthiessen and Foster, was formed under the influence of the last-named agent.

On fusing hydrocotarnine with potash, much charring took place at 200—210°: an aqueous liquid distilled over, together with a heavy colourless oil; the latter solidified on standing to a mass of crystals; these melted at 55°, and gave a platinum salt, of which 0·8005 gram gave 0·1865 Pt. = 23·29 per cent.

Calculated for hydrocotarnine platinochloride 23·11 per cent.

In all respects these crystals corresponded with the original hydrocotarnine; whence it seems that this base can be distilled with only partial decomposition.

The aqueous liquid was distilled with potash, and the distillate collected in dilute hydrochloric acid; the solution was evaporated to dryness; and the residue treated with absolute alcohol. Sal-ammoniac was thus left undissolved, and a salt dissolved out from which a platinochloride was prepared: of this

0·4930 gram gave 0·2080 pt. = 42·19 per cent.
Methylamine platinochloride requires 41·63 „

Only methylamine could be detected qualitatively in this salt by the odour on adding potash: hence apparently no pyridine or other analogous bases were formed.

The residue left in the retort in which the fusion was performed gave, on solution in water and treatment with hydrochloric acid and ether, a small quantity of extract which refused to crystallise distinctly, although it exhibited indications of crystallisation; this substance dissolved in water, forming a solution which gave a copious whitish precipitate with lead acetate, and with ferric chloride struck a greenish-brown colour, becoming purple-black with ammonia: the amount of this decomposition-product was too small for examination.

Matthiessen and Foster have shown that by the action of hydracids on cotarnine, methyl is eliminated as chloride, &c.; and as pointed out in Part II, Appendix B, this action rather tends to show that the methyl group must be regarded as associated thus, $(C_{11}H_{10}NO_2).OCH_3$, and not thus, $(C_{11}H_{10}O_3).N.CH_3$, as written by Matthiessen and Foster. This conclusion is somewhat strengthened by the negative results of attempts to act with nitrous acid on the product of the action of hydriodic acid on hydrocotarnine. From 30 grams of hydrocotarnine and 90 of 50 per cent. hydriodic acid gently boiled together, there were collected 16·5 grams of methyl iodide, the theoretical yield from $C_{12}H_{15}NO_3.\frac{1}{2}H_2O$ being 18·5; wherefore about 90 per cent. of the theoretical yield was actually collected. The product appeared, unlike the "hydriodide of cotarnamic acid" obtainable from cotarnine by similar treatment, to be incapable of forming crystals or of yielding a crystalline hydrochloride when heated with hydrochloric acid; on treatment with nitrous acid in various ways, it yielded no substance capable of isolation in a state of purity, except a small quantity of oxalic acid; a little of some volatile compound producing profuse lachrymation was extracted or formed on treating the products of the actions with ether. Were the formula $C_{11}H_{12}O_3.NCH_3$ applicable to hydrocotarnine, the product of the action of hydriodic acid would probably be $C_{11}H_{12}O_3.NH$; and from this product the elimination of the nitrogen by nitrous acid might be anticipated.

On fusing together hydrocotarnine and opianic acid at various temperatures, the reaction—

$$C_{12}H_{15}NO_3 + C_{10}H_{10}O_5 = H_2O + C_{22}H_{23}NO_7$$

did *not* take place, and no narcotine was formed. At 150—160° the hydrocotarnine was partly decomposed, and by the action of the nascent decomposition-products on the opianic acid, *meconin* was formed in some quantity, upwards of half of the opianic acid being thus converted in a few minutes; the reducing action of the decomposition-products of the hydrocotarnine was thus precisely the same as that observed when narcotine was split up into hydrocotarnine and opianic acid by heating with water in sealed tubes at 150° (Part 1) in accordance with the above equation when inverted, much meconin and very little hydrocotarnine being thus obtained after several hours' heating.

§ 2. *Action of Bromine on Hydrocotarnine Hydrobromide.*

In the hope of possibly obtaining a splitting up of cotarnine and hydrocotarnine under the influence of bromine, the effect of this reagent on these bases was examined, and thereby some interesting results obtained, though not altogether of the kind hoped for.

When hydrocotarnine is dissolved in dilute hydrobromic acid, and the solution treated with bromine-water, different products are formed according to the temperature and strength of the solution, the quantity of bromine employed, and the rate at which it is added; and much perplexity was caused by these differences before the exact character of the reactions occurring was made out. If to a cold solution of cotarnine in hydrobromic acid bromine-water be gently added, a yellowish-white precipitate is formed which almost instantaneously redissolves on agitation; this precipitate is apparently produced by the combination of bromine with hydrocotarnine, thus—

$$(1.)\qquad C_{12}H_{15}NO_3,HBr + Br_2 = C_{12}H_{15}Br_2NO_3.HBr,$$

and its solution is due to its rapidly breaking up into hydrobromic acid and *bromhydrocotarnine hydrobromide*, thus—

$$(2.)\qquad C_{12}H_{15}Br_2NO_3,HBr = HBr + C_{12}H_{14}BrNO_3,HBr.$$

When the whole of the hydrocotarnine has thus been transformed into bromhydrocotarnine, the addition of a little more bromine gives rise to a precipitate much more permanent than the former one, although on standing in contact with water for a few minutes or longer, according to the amount of the precipitate, this new precipitate also disappears: this second precipitate, however, is so far permanent that it can readily be determined when just enough bromine has been added to convert the hydrocotarnine wholly into bromhydrocotarnine, by the turbidity remaining for a few moments after agitation, whilst the compound formed can be isolated, though with difficulty.

The comparatively permanent precipitate thus produced is formed by the direct addition of bromine to bromhydrocotarnine, thus—

$$(3.) \qquad C_{12}H_{14}BrNO_3,HBr + Br_2 = C_{12}H_{14}Br_3NO_3,HBr,$$

and its disappearance on standing is due to its breaking up into two equivalents of hydrobromic acid and *bromocotarnine hydrobromide*, thus—

$$(4.) \qquad C_{12}H_{14}Br_3NO_3,HBr = 2HBr + C_{12}H_{12}BrNO_3,HBr.$$

By adding to hydrocotarnine hydrobromide enough bromine to convert it wholly into bromhydrocotarnine hydrobromide, and then just as much more bromine, and gently warming the whole until clear, bromocotarnine hydrobromide can be obtained in almost the theoretical quantity.

If finally to the clear solution of bromocotarnine hydrobromide two more proportions of bromine be added, a yellow crystalline precipitate is thrown down which does not redissolve on standing for some time in the cold, although it is profoundly altered by continued boiling with water; this precipitate is the addition-product formed by the reaction—

$$(5.) \qquad C_{12}H_{12}BrNO_3,HBr + Br_2 = C_{12}H_{12}Br_3NO_3,HBr,$$

and may accordingly be termed *tribromhydrocotarnine hydrobromide*. This body is sufficiently stable to bear washing and drying over sulphuric acid, and when quite dry may be heated to 100° for two or three hours with only inconsiderable loss of weight; long-continued heating at 100°, however, causes the elements of hydrobromic acid to be expelled, whilst at higher temperatures yet more profound changes are produced.

It is noticeable that the three addition-products, $C_{12}H_{15}Br_2NO_3,HBr$, $C_{12}H_{14}Br_3NO_3,HBr$, and $C_{12}H_{12}Br_3NO_3,HBr$, thus successively formed possess a gradually increasing stability; the first decomposes almost as rapidly as formed; the second, though decomposing in contact with water in the course of a short time, is yet sufficiently stable to be isolated, as shown below: whilst the third is quite permanent.

The following is the experimental evidence from which the above conclusions are drawn:—

(A.) *Preparation of Hydrocotarnine Hydrobromide and of Bromhydrocotarnine Hydrobromide therefrom.*

The hydrobromide of hydrocotarnine is considerably less soluble in water than the hydrochloride, and hence may with advantage be used instead in the process of purifying crude hydrocotarnine by conversion into a salt, and recrystallising the latter as described in Part I. When dried in blotting-paper by pressure, the crystallised salt gave these numbers—

1·0725 gram lost at 100° 0·0955 gram = 8·90 per cent.
Calculated for $C_{12}H_{15}NO_3,HBr,1\frac{1}{2}H_2O$ = 8·21 ,,
0·9770 gram of dry salt gave 0·6115 AgBr Br = 26·63 ,,
Calculated for $C_{12}H_{16}NO_3,HBr$ = 26·49 ,,

When hydrocotarnine hydrobromide is dissolved in water, and bromine-water gently added until the precipitate formed just ceases to redissolve on agitation, the reactions indicated by equations (1) and (2) above are completed, equivalent quantities of bromhydrocotarnine hydrobromide and of hydrobromic acid being formed. To verify this quantitatively, bromine-water of accurately known strength was added to weighed quantities of pure anhydrous hydrocotarnine hydrobromide dissolved in about 100 parts of water; and the hydrobromic acid set free after the completion of the reaction was determined by a standard soda-solution, a few drops of cochineal tincture being employed as indicator: this colouring matter is very suitable for such purposes where heating must be avoided, it is not affected by carbonic acid.

0·5210 gram of anhydrous salt thus required 0·2777 gram of bromine, and generated 0·1440 gram of hydrobromic acid.

In another experiment 0·4620 gram required 0·2448 bromine, and formed 0·1310 hydrobromic acid.

	Calculated.	Observed.	
Bromine per 100 parts of anhydrous salt ..	52·98	53·30	52·99
Hydrobromic acid, ditto, ditto............	26·82	27·64	28·35

On concentrating the solutions of bromhydrocotarnine hydrobromide thus obtained and leaving them at rest, crystals separated which, when purified by recrystallisation, yielded the following numbers. The bromine in this and the other brominated compounds described below was determined by boiling for half an hour with excess of silver nitrate and nitric acid diluted with two parts of water; filtering off and evaporating the filtrate almost to dryness; taking up with water; filtering from very small quantity of silver bromide; and again evaporating the filtrate with addition of nitric acid, and so on until no more silver bromide was formed during the evaporation. Usually, though not always, almost the whole of the silver bromide obtained was formed during the first boiling, only small quantities being produced during the evaporation to dryness of the first filtrate, and not more than traces during the second. The brominated cotarnine derivatives described in this paper are far less easily broken up by silver nitrate and nitric acid than iodised and brominated morphine and codeine derivatives, which yield every trace of their bromine or iodine as silver-compound on a few minutes' boiling with acid silver nitrate.

Bromhydrocotarnine hydrobromide when air-dry loses no weight at 100°, and is therefore anhydrous: 0·3365 gram gave 0·4530 CO_2 and 0·1290 H_2O.

0·6300 gram gave 0·6165 AgBr.

	Calculated.		Found.
C_{12}	144	37·79	36·72
H_{15}	15	3·94	4·26
Br_2	160	41·99	41·65
N	14	3·68	—
O_3	48	12·60	—
$C_{12}H_{14}BrNO_3,HBr$.	381	100·00	

On adding caustic potash to the aqueous solution of the hydrobromide, a milky precipitate is thrown down, soon becoming crystalline, and much resembling hydrocotarnine; this is soluble in ether with great ease, and crystallisable therefrom in crystals much resembling hydrocotarnine, but melting at 76° (*corrected*), or some 20° higher: they further differ from hydrocotarnine in being anhydrous (hydrocotarnine is $C_{12}H_{15}NO_3,\frac{1}{2}H_2O$).

0·2190 gram gave 0·3780 CO_2 and 0·0940 H_2O.

	Calculated.		Found.
C_{12}	144	48·00	47·08
H_{14}	14	4·67	4·76
Br	80	26·66	—
N	14	4·67	—
O_3	48	16·00	—
$C_{12}H_{14}BrNO_3$....	300	100·00	

The platinum salt is crystalline; it gave the following numbers:

0·4520 gram gave 0·0880 Pt. = 19·47 per cent.
Calculated for $(C_{12}H_{14}BrNO_3,HCl)_2PtCl_4$ = 19·51 „

(B.) *Preparation of Bromocotarnine Hydrobromide.*

In order to verify equation (3), anhydrous hydrocotarnine hydrobromide was treated with just sufficient bromine-water to convert it wholly into bromhydrocotarnine hydrobromide; as much more bromine-water was then added, whereby a yellow precipitate was thrown down, wihch partly redissolved on standing for a few minutes, the remainder becoming crystalline. The crystals were rapidly filtered off, washed, drained, and dried over sulphuric acid: on analysis they gave numbers agreeing with the formula $C_{12}H_{14}Br_3NO_3,HBr$.

0·3910 gram gave 0·3730 CO_2 and 0·0980 H_2O.
0·3300 „ 0·4500 AgBr.

	Calculated.		Found.
C_{12}..............	144	26·62	26·02
H_{15}..............	15	2·77	2·78
Br_4..............	320	59·15	58·02
N..............	14	2·59	—
O_3..............	48	8·87	—
$C_{12}H_{14}Br_3NO_3,HBr$	541	100·00	

To verify equation (4), weighed quantities of hydrocotarnine hydrobromide and of bromhydrocotarnine hydrobromide were dissolved in water, and treated with bromine-water of known strength in quantities sufficient to bring about reactions 1, 2, 3, and 4 jointly, and reactions 3 and 4 in each case respectively. After becoming clear by standing for some hours, the amounts of hydrobromic acid formed were titrated as above described.

0·521 gram anhydrous hydrocotarnine hydrobromide gave 0·4110 HBr = 78·89 per cent.

0·4620 gram anhydrous hydrocotarnine hydrobromide gave 0·3685 HBr = 79·77 per cent.

Calculated, 80·46 per cent.

0·790 gram anhydrous bromhydrocotarnine hydrobromide gave 0·3200 HBr = 40·51 per cent.

0·803 gram anhydrous bromhydrocotarnine hydrobromide gave 0·3430 HBr = 42·71 per cent.

Calculated, 42·52 per cent.

The bromocotarnine thus formed was isolated by adding potash, agitating with ether, and spontaneously evaporating the ethereal solution; crystals much resembling those of cotarnine were thus obtained containing $C_{12}H_{12}BrNO_3,H_2O$; these fused at 100°, losing the water of crystallisation and becoming brown and slightly decomposed.

0·2470 dried over sulphuric acid gave 0·4095 CO_2, and 0·1010 H_2O.

	Calculated.		Found.
C_{12}	144	45·57	45·22
H_{14}............	14	4·43	4·54
Br.............	80	25·32	—
N	14	4·43	—
O_4.............	64	20·25	—
$C_{12}H_{12}BrNO_3,H_2O$	316	100·00	

0·2775 gram of anhydrous crystals lost at 100°, 0·0225 = 8·10 per cent.

0·2605 gram of anhydrous crystals lost at 100°, 0·0215 = 8·25 per cent.

Calculated = 5·69 per cent.

The increased loss at 100° is clearly due to slight decomposition, the crystals becoming a brown resinous mass on fusing.

0·2390 gram dried at 100° gave 0·1465 AgBr; Br = 26·08 per cent.

Calculated for $C_{12}H_{12}BrNO_3$, 26·84 per cent.

Bromocotarnine forms well-crystallised, easily soluble salts; like cotarnine, it is precipitated by caustic alkalis, but not by their carbonates: it is only moderately soluble in cold ether or benzene, but is readily dissolved by hot alcohol or benzene; boiling with alcohol, however, converts it to some extent into a tarry non-crystalline mass.

On solution in dilute hydrobromic acid and evaporation over sulphuric acid, a well-crystallised hydrobromide is obtained, much resembling cotarnine hydrobromide: after purification by two successive recrystallisations, the following numbers were obtained :—

0·731 gram of air-dry salt lost at 100°, 0·039 gram, or 5·33 per cent.

Calculated for $C_{12}H_{12}BrNO_3,HBr,H_2O$ = 4·53 per cent.

0·692 gram of dried salt gave 0·682 AgBr Br = 41·94 per cent.

Calculated for $C_{12}H_{12}BrNO_3,HBr$ = 42·22 per cent.

The platinum salt is a yellow crystalline powder readily obtained by adding $PtCl_4$ to a solution of the base in HCl.

0·6885 gram gave 0·1350 Pt = 19·61

Calculated $(C_{12}H_{12}BrNO_3,HCl)_2PtCl_4$ = 19·60.

(C.)—*Preparation of Tribromhydrocotarnine Hydrobromide.*

By cautiously adding bromine-water to hydrocotarnine hydrobromide until a permanent precipitate just begins to appear, then adding as much more bromine-water and leaving the mixture for an hour or two, until the precipitate has re-dissolved, and finally adding a third equal quantity of bromine-water (or, preferably, a slight excess, as a little bromine appears to be used up in subsidiary reactions), a yellow precipitate of fine crystals is obtained, consisting of tribromhydrocotarnine hydrobromide. The same product is also formed if, instead of hydrocotarnine, bromhydrocotarnine be used, and bromine enough to bring about reactions (3 and 4) above be added, just as much more bromine (or preferably a slight excess) being further added after the lapse of an hour or two, when the first precipitate has re-dissolved; and finally the same product is yet again obtained if bromocotarnine hydrobromide be dissolved in water, and a slight excess of bromine-water added thereto. The following numbers were obtained with the fine crystals, well washed, and dried over sulphuric acid. In order to determine the bromine, it was found necessary to add to the weighed quantity of substance NH_3, then excess of $AgNO_3$, and finally NO_3H, and to boil, &c., as above described. On addition of $AgNO_3$ to the original without NH_3, Br was evolved.

A. From hydrocotarnine, 0·3785 gram gave 0·3695 CO_2 and 0·0870 H_2O.

0·3540 gram gave 0·4910 AgBr.

B. From bromhydrocotarnine, 0·4065 gram gave 0·3890 CO_2 and 0·0920 H_2O. 0·5610 gram gave 0·7775 AgBr.

C. From bromocotarnine, 0·5785 gram gave 0·5595 CO_2 and 0·1290 H_2O.

0·4365 gram gave 0·6130 AgBr.

	Calculated.		Found.		
			A.	B.	C.
C_{12}..............	144	26·71	26·62	26·10	26·38
H_{13}..............	13	2·41	2·55	2·51	2·48
Br_4..............	320	59·37	59·02	58·98	59·77
N..............	14	2·60	—	—	—
O_3..............	48	8·91	—	—	—
$C_{12}H_{12}Br_3NO_3,HBr$	539	100·00			

When hydrocotarnine hydrobromide solution is dropped into a considerable excess of bromine-water, an orange-coloured tarry precipitate falls, which, on standing, becomes converted into an orange-yellow crystalline mass of tribromhydrocotarnine hydrobromide. A specimen thus prepared contained carbon, 27·27; hydrogen, 2·56; after drying over sulphuric acid.

Calculated, carbon, 26·71; hydrogen, 2·41.

§ 3.—*Derivatives of Bromocotarnine.*

(A.) *Action of Nascent Hydrogen on Bromocotarnine.*

When bromocotarnine, prepared as above described, is dissolved in hydrochloric acid, and zinc is added to the solution so as keep up a gentle evolution of hydrogen for two days, *bromhydrocotarnine* is formed, identical with that derived from hydrocotarnine by bromination (§ 2 A), the reaction being—

$$C_{12}H_{12}BrNO_3 + H_2 = C_{12}H_{14}BrNO_3,$$

precisely parallel with that whereby hydrocotarnine is formed from cotarnine. By adding a large excess of ammonia to the resulting solution, and agitating with ether, the new base is separated from the zinc chloride, and by agitating the ethereal solution with dilute hydrobromic acid, a magma of crystals of bromhydrocotarnine hydrobromide is obtained. After recrystallisation, these gave the following results: the crystals, when air-dry, were anhydrous. 0·3600 gram gave 0·4955 CO_2 and 0·1360 H_2O.

	Calculated.		Found.
C_{12}	144	37·79	37·54
H_{15}	15	3·94	4·19
Br_2	160	41·99	—
N	14	3·68	—
O_3	48	12·60	—
$C_{12}H_{14}BrNO_3,HBr$	381	100·00	

The free base was prepared by adding caustic potash to the hydrobromide and crystallising from ether; it precisely resembled that from hydrocotarnine in all its properties; it was anhydrous when air-dry, and melted at 78° (*corrected*).

0·3550 gram gave 0·6355 CO_2 and 0·1600 H_2O.

	Calculated.		Found.
C_{12}	144	48·00	48·82
H_{14}	14	4·67	5·01
Br	80	26·66	—
N	14	4·67	—
O_3	48	16·00	—
$C_{12}H_{14}BrNO_3$	300	100·00	

It hence results that the same substance is formed by adding hydrogen to cotarnine (forming hydrocotarnine) and brominating the product, as is produced by brominating cotarnine (forming bromocotarnine), and hydrogenising the product.

(B.) *Action of Heat on Bromocotarnine Hydrobromide.*

When anhydrous bromocotarnine hydrobromide is heated to 190—210°, it decomposes, evolving hydrobromic acid and combustible vapours, leaving behind a greenish-blue mass containing the hydrobromides of two bases, one of which is probably formed by the elimination of methyl bromide in accordance with the equation—

$$C_{12}H_{12}BrNO_3HBr = CH_3Br + C_{11}H_9NO_3,HBr,$$

whilst the other is produced by a further alteration of the salt thus formed.

On boiling with alcohol the product of the heating, blue flakes are left undissolved in large quantity, whilst yellowish-brown resinous bye-products and the hydrobromide of the first base are dissolved. By evaporating down the alcoholic solution, taking up the residue with water, and fractionally precipitating with caustic soda, a nearly white base was obtained, but in too minute quantity for complete study; the salts of the base did not appear to crystallise readily; they are precipitated by caustic fixed alkalis, but not by their carbonates. The platinum-salt gave the following numbers:—

0·0775 gram gave 0·0185 Pt .... = 23·87 per cent.
Calculated for $(C_{11}H_9NO_3,HCl)PtCl_4$ = 24·14 „

To this base it is proposed to assign the name *tarconine* (anagram on cotarnine and on narcotine). Although tarconine itself is of but little consequence on account of the difficulty of preparation, its brominated derivative, $C_{11}H_8BrNO_3$, *bromotarconine*, is, as will be described later on, a well-marked base, possessed of rather striking peculiarities (§ 4 B).

The blue flakes thus left undissolved in alcohol are, apparently, the hydrobromide, or basic hydrobromide, of a peculiar base, of formula $C_{20}H_{14}N_2O_6$: they are almost insoluble in all the ordinary menstrua; in alcohol, ether, benzene, petroleum, glycerine, turpentine, and carbon disulphide, they are quite insoluble; in boiling water they dissolve to an infinitesimal extent, yielding a violet liquid; boiling glacial acetic acid and boiling aniline dissolve them to a small extent, forming deep-blue liquids; concentrated hydrobromic acid partially dissolves to a purple-violet fluid. From none of these bodies can the substance be crystallised; but on boiling with a very large bulk of distilled water strongly acidulated with acetic acid, and evaporating down the deep blue filtered solution, indistinctly crystalline flakes separate, exactly resembling indigo in appearance, and possessing the same coppery lustre when dry. These flakes gave numbers agreeing best with the formula $4C_{20}H_{14}N_2O_6,3HBr$.

0·3170 gram gave 0·6255 CO_2 and 0·1150 H_2O.
0·5540 „ 0·1715 AgBr.

	Calculated for above formula.	Found.
Carbon	54·70	53·81
Hydrogen	3·36	4·03
Bromine........	13·67	13·17

On treating the original blue flakes with strong sulphuric acid, they dissolved with evolution of hydrobromic acid, forming an intensely-tinted magenta-coloured solution: the tinctorial power of the substance in sulphuric acid solution rivals that of the rosaniline-derivatives, a very minute speck giving a deep colour to a considerable quantity of acid. On adding water to the magenta-coloured fluid, chocolate-brown flakes precipitate, becoming blue and coppery after washing and drying; the flakes thus prepared, after another solution in strong sulphuric acid (distilled so as to separate lead sulphate, &c.), and precipitation by water, consist of the sulphate $(C_{20}H_{14}N_2O_6)_2,H_2SO_4$; the following numbers were obtained with the perfectly drained and washed substances:—

0·2480 gram of the sulphate gave 0·5070 CO_2 and 0·0870 H_2O.
0·3175 „ „ „ 0·6495 „ 0·1090 „
0·450 „ „ burnt with soda-lime gave 0·2030 Pt.
0·6760 „ „ with $Ba(NO_3)_2$ and HNO_3 „ 0·1785 $BaSO_4$.

	Calculated.		Found.	
C_{40}	480	56·21	55·75	55·79
H_{30}..	30	3·51	3·89	3·81
N_4...............	56	6·55	6·39	
S	32	3·75	3·63	
O_{16}..............	256	29·98	—	—
$(C_{20}H_{14}N_2O_6)_2H_2SO_4$	854	100·00		

On rubbing up this sulphate in a mortar with ammonia solution, black humus-like flakes of the free base are produced; these are excessively difficult to filter even with the aid of the Bunsen-pump. When dry, they form a friable indigo-blue mass of coppery lustre, much resembling the hydrobromide and sulphate: on treatment with sulphuric acid, they dissolve to a magenta-coloured liquid; with hydrobromic acid, they form a violet-purple solution.

This new product is formed in quantity when tarconine hydrobromide or hydrochloride is heated to about 200°: it would seem that it is formed from tarconine by duplication and elimination of the elements of olefiant gas; but little stress, however, can be laid on this connection, as all the brominated hydrocotarnine-derivatives yield the blue substance in greater or less quantity, and along with more or less bye-products on heating to about 200°.

It is noteworthy that the acid-saturating power of the base is only half that due to the nitrogen present; *i.e.*, although di-nitrogenous, it is only monoacid.

§ 4. *Derivatives of Tribromhydrocotarnine Hydrobromide.*

(A.) *Action of Water at 100° on Tribromhydrocotarnine Hydrobromide.*

When pure tribromhydrocotarnine hydrobromide is boiled with water for half-an-hour or less, according to the quantities employed, it dissolves to a yellow-orange fluid, much hydrobromic acid being liberated in so doing. It would naturally be expected, from the character of the reactions undergone by the action of water on the addition-products, $C_{12}H_{15}Br_2NO_3,HBr$ and $C_{12}H_{14}Br_3NO_3,HBr$ (formed respectively from hydrocotarnine and bromhydrocotarnine hybromides by addition of bromine), that this action would be expressed by the equation—

$$(1.) \qquad C_{12}H_{12}Br_3NO_3,HBr = HBr + C_{13}H_{11}Br_2NO_3,HBr;$$

i.e., that *dibromocotarnine hydrobromide* would be formed. The quantity of hydrobromic acid set free, however, is uniformly in considerable excess of the amount thus indicated; whilst the resulting-product appears to be not a single body, but a mixture of two hydrobromides, of which one appears to be incapable of crystallising, whilst the other is simply bromocotarnine hydrobromide: the action appears, therefore, to be of an abnormal character, and is probably expressed by the equation—

$$(2.) \qquad 2C_{12}H_{12}Br_3NO_3,HBr = 3HBr + C_{12}H_{12}BrNO_3,HBr + \\ C_{12}H_9Br_2NO_3,HBr.$$

The following values were obtained:—

1·005 gram of tribromhydrocotarnine hydrobromide (prepared from pure bromocotarnine hydrobromide and bromine) gave, after boiling with water till dissolved—

0·2502 gram HBr (estimated by titration) HBr = 24·92 per cent.
0·5250 „ gram gave 0·1187 gram HBr .... = 22·61 „
Calculated for reaction (2) .... = 22·54 „

The solution of hydrobromides thus obtained dried up on standing over sulphuric acid to a varnish-like mass, through which a few crystals were interspersed, but on account of the solubility of these, they could not be separated from the non-crystalline salt: after drying at 100°, the mass contained carbon, 34·24; hydrogen, 3·34; whilst a mixture of bromocotarnine hydrobromide and the product, $C_{12}H_9Br_2NO_3,HBr$, indicated by the above equation, would require carbon, 34·49; hydrogen, 2·78. On solution in water, and addition of caustic potash, a precipitate was obtained, rapidly becoming crystalline (sodium carbonate and ammonia yielded no precipitates); by fractionally crystallising the solution of the mixed bases thus thrown down from ether, a crop of crystals of almost pure bromocotarnine were obtained, the mother-liquor drying up to a varnish much richer in bromine. These crystals gave the following numbers:—

0·3365 gram gave 0·5530 CO_2, and 0·1410 H_2O.
0·2320 „ 0·1410 AgBr.

	Calculated.		Found.
C_{12}	144	45·57	44·82
H_{14}	14	4·43	4·65
Br.............	80	25·32	25·86
N	14	4·43	—
O_4.............	64	20·25	—
$C_{12}H_{12}BrNO_3,H_2O$	316	100·00	

When dried at 100°, these crystals fused to a reddish resin losing 7·87 per cent. (calculated 5·69, *vide* § 2, B); on treatment with zinc and hydrochloric acid, they furnished bromhydrocotarnine identical with that above described.

(B.) *Action of Alkalis and of Silver Hydrate on Tribromhydrocotarnine Hydrobromide.*

Attempts to prepare dibromocotarnine by acting on tribromhydrocotarnine hydrobromide with alkalis and with silver hydrate (the latter being suspended in alcohol), did not lead to the desired result; nothing but bromocotarnine and uncrystallisable bye-products could be thus obtained. By treating tribromhydrocotarnine hydrobromide with dilute caustic potash, a tarry substance is produced, from which bromocotarnine can be isolated by solution in dilute hydrobromic acid, filtration from resinous matters, and treatment with potash and ether, and fractional crystallisation from ether, the last crystals containing more or less admixture of non-crystalline bodies mechanically adherent.

Similarly by treating tribromhydrocotarnine hydrobromide with silver hydrate suspended in alcohol, much silver bromide was formed, and an alcoholic solution from which bromocotarnine was obtained by acidulating, evaporating to a small bulk, solution in water, filtration from resin, and treatment with potash and ether.

The crystals thus obtained gave the following numbers after drying at 100°, when they fused to resinous masses:—

(A.) By caustic potash 0·3335 gram gave 0·5950 CO_2 and 0·1360 H_2O.
(B.) By silver hydrate 0·2550 „ 0·4565 „ 0·1110 „

	Calculated.		Found.	
			A.	B.
C_{12}	144	48·32	48·65	48·82
H_{12}	12	4·03	4·53	4·83
Br	80	26·84	—	—
N	14	4·70	—	—
O_3	48	16·11	—	—
$C_{12}H_{12}BrNO_3$	298	100·00		

(C.) *Action of Heat on Tribromhydrocotarnine Hydrobromide.*

When tribromhydrocotarnine hydrobromide, dried over sulphuric acid, is kept at 100° for several days, it slowly loses weight, hydrobromic acid being expelled. At the end of a week, the whole is soluble in cold water, with a brown-green colour. The aqueous solution contains, besides other products, bromocotarnine, which can be extracted by precipitating with potash and treating with ether. The platinum salt of bromocotarnine thus obtained gave these numbers:—

0·4750 gram gave 0·0935 Pt.......... = 19·68 per cent.
Calculated for $(C_{12}H_{12}BrNO_3,HCl)_2PtCl_4$ = 19·60 „

At a temperature of 180—200°, tribromhydrocotarnine hydrobromide splits up in quite a different fashion. On cautiously heating it melts and evolves methyl bromide and hydrobromic acid, and forms the hydrobromide of a brominated base $C_{11}H_8BrNO_3$, in accordance with the equation—

$$C_{12}H_{12}Br_3NO_3,HBr = HBr + CH_3Br + C_{11}H_8BrNO_3,HBr.$$

This new base is manifestly the monobrominated derivative of the *tarconine* $C_{11}H_9NO_3$ above described (§ 3, B.), and may accordingly be termed *Bromotarconine.* In order to verify the above equation, the vapours evolved on heating tribromhydrocotarnine hydrobromide (dried over sulphuric acid) to 180—200° were passed through a red-hot combustion-tube containing lead chromate, and the carbon dioxide produced was collected in the usual way. It was found, however, that a trace of carbon dioxide was evolved as a subsidiary product during the reaction, the gases evolved rendering baryta-water turbid. This was estimated in a separate portion by heating and passing the evolved vapours through a U-tube, containing fragments of glass moistened with water, then through a calcium chloride tube, and finally into a potash bulb. In this way the following numbers were obtained on burning the vapours with lead chromate:—

Specimen A. 1·155 gram gave 0·0900 CO_2 and 0·0675 H_2O.
„ B. 1·900 „ 0·1450 CO_2 „ 0·115 „
„ C. 3·460 „ 0·2670 CO_2.

whilst the following values were obtained for the CO_2, evolved as such:—

Specimen B. 5·100 gram gave 0·0230 CO_2.
„ C. 5·700 „ 0·0380 „

	Total carbon in vapours.	Hydrogen in vapours.	Carbon as CO_2 in vapours.
A................	2·13	0·65	—
B................	2·08	0·67	0·12
C................	2·11	—	0·18
Mean	2·11	0·66	0·15

Hence deducting the carbon present as CO_2 in the vapours from the total, the mean numbers found are :—

	Calculated.	Observed.
Carbon	2·22	1·96
Hydrogen	0·74	0·66

The observed numbers, therefore, agree sufficiently closely with those calculated to show that the main reaction taking place is that above indicated.

Bromotarconine hydrobromide is readily obtained from the product of the reaction, by boiling the residue with alcohol, and filtering hot. On cooling, greenish crystals of the salt are deposited. These are digested with hot water and animal charcoal, and after two or three recrystallisations form light straw-yellow crystals; or the crude crystals may be dissolved in water, and the filtered solution precipitated by sodium carbonate. The dirty orange-scarlet precipitate of base is then crystallised from alcohol, and converted into the required salt. This process may also be applied to the crude product of the heating to 170—180°; a little sodium carbonate solution is well mixed with the product, and the whole then boiled with alcohol, whereby free bromotarconine is dissolved out and crystallises out on cooling. The following numbers were obtained:—

Hydrobromide of Bromotarconine.—Specimen crystallised from 90 per cent. spirit, and dried in the air till constant.

0·3500 gram lost at 100° 0·0160 .... = 4·57 per cent.
0·4475 „ „ 0·0195 .... = 4·36 „
Calculated for $C_{11}H_8BrNO_3,HBr,H_2O$ .... 4·72 „

Specimen crystallised from water: Air-dry.

0·7000 gram lost at 100° 0·0620 .... = 8·87 „
Calculated for $C_{11}H_8BrNO_3,HBr,2H_2O$ .... = 9·02 „
0·3320 gram of salt dried at 100° gave 0·4435 CO_2 and 0·082 H_2O.
0·4270 „ „ „ 0·4370 AgBr.

	Calculated.		Found.
C_{11}	132	36·36	36·43
H_9	9	2·48	2·74
Br_2............	160	44·08	43·55
N............	14	3·86	—
O_3............	48	13·22	—
$C_{11}H_8BrNO_3,HBr$	363	100·00	

This salt crystallises in micaceous glistening straw-yellow scales, not very soluble in cold water or alcohol, but dissolving pretty readily in each solvent, when hot, to a slightly orange-yellow solution. At 180—200° it undergoes no change, but at about 280° it slowly loses weight, leaving a residue containing a large quantity of the blue substance formed by the decomposition of tarconine hydrobromide. (*Vide* § 3, B.)

Free Bromotarconine. — As precipitated by sodium carbonate or ammonia from a not too dilute warm solution of any of its salts, hydrated crystals are obtained of a bright orange-scarlet hue; these crystallise unchanged from 80 per cent. alcohol. At 100° they become anhydrous, changing in colour to crimson. These crimson crystals, on solution in hot alcohol, containing a minute quantity of water only, separate out on cooling as the orange hydrated crystals, and consequently bromotarconine may be used as a test of the "absoluteness" of alcohol. The base is insoluble in ether.

0·5680 gram of air-dry orange crystals lost at 100° 0·0630 = 11·09 per cent.

0·3860 gram of air-dry orange crystals lost at 100° 0·0440 = 11·40 per cent.

Calculated for $C_{11}H_8BrNO_3,2H_2O$ = 11·32 per cent.
0·3420 gram of dried base gave 0·5925 CO_2 and 0·095 H_2O.
0·4870 „ „ „ 0·3260 AgBr.

	Calculated.		Found.
C_{11}............	132	46·81	47·24
H_8............	8	2·84	3·08
Br............	80	28·37	28·48
N	14	4·96	—
O_3............	48	17·02	—
$C_{11}H_8BrNO_3$....	282	100·00	

When cautiously heated, free bromotarconine chars, giving off a disagreeable odour, without forming more than traces of the blue product referred to above.

Hydrochloride of Bromotarconine.—This salt much resembles the hydrobromide, and is readily obtained.by dissolving the base in warm dilute hydrochloric acid, and crystallising.

0·7820 gram of air-day crystals lost at 100° 0·0850 = 10·87 per cent.
Calculated for $C_{11}H_8BrNO_3HCl,2H_2O$ .... = 10·16 „

0·5810 gram of dried salt gave 0·6050 gram of mixed AgCl and AgBr. Mixed silver salts........................ 104·13 per cent.
Calculated .... 104·08 „

0·388 gram dried at 100° gave 0·5940 CO_2 and 0·1050 H_2O.

	Calculated for $C_{11}H_8BrNO_3$,HCl.	Found.
Carbon............	41·45	41·75
Hydrogen	2·83	3·01

On heating to a higher temperature, this salt formed the blue base above described $C_{20}H_{14}N_2O_6$, in considerable quantity.

Bromotarconine platinochloride.—On adding platinic chloride to a solution of bromotarconine hydrochloride, a crystalline yellow precipitate is thrown down. After drying over sulphuric acid and finally at 100°, the following numbers were obtained; the salt fuses on heating and swells up enormously, forming an indigo-like mass, containing a large quantity of the blue product described above (§ 3, B.).

A. Platinochloride from tribromocotarnine prepared from bromhydrocotarnine.

B. Platinochloride from tribromocotarnine prepared from bromocotarnine.

A. 0·3305 gram gave 0·0665 Pt ...... = 20·12
B. 0·4810 „ 0·0960 .... = 19·96
Calculated for $(C_{11}H_8BrNO_3,HCl)PtCl_4$ = 20·23

§ 5. *Action of Bromine on Cotarnine Hydrobromide.*

From the results above detailed obtained with hydrocotarnine, it might be inferred that the first action of bromine on cotarnine hydrobromide would be a direct combination forming one of the additive products $C_{12}H_{13}Br_2NO_3,HBr$, or $C_{12}H_{13}Br_4NO_3,HBr$; and that subsequently these substances would split up with the evolution of hydrobromic acid, the former producing bromocotarnine, and the latter probably tribromhydrocotarnine hydrobromide. Thus:

(1.) $C_{12}H_{13}Br_2NO_3,HBr = HBr + C_{12}H_{12}BrNO_3,HBr.$
(2.) $C_{12}H_{13}Br_4NO_3,HBr = HBr + C_{13}H_{12}Br_3NO_3,HBr.$

In point of fact, all these reactions appear to occur. When a slight excess of bromine is added to a strong solution of cotarnine hydrobromide, an orange tarry precipitate is thrown down, which becomes crystalline on standing. After washing with water and drying over sulphuric acid, this substance appears to be a variable mixture of the addition product $C_{12}H_{13}Br_2NO_3,HBr$ (which may be termed *dibromhydrocotarnine hydrobromide*), and of tribromhydrocotarnine hydrocotarnine hydrobromide produced from the second addition product $C_{12}H_{13}Br_4NO_3,HBr$ by reaction (2) above. Equation (1) is realised on boiling with water the crystalline mass, bromocotarnine being thus readily obtainable in a state of tolerable purity.

Cotarnine hydrobromide was prepared as starting point by dissolving cotarnine crystallised from benzene in dilute hydrobromic acid, and concentrating the solution. On cooling and standing, especially over sulphuric acid, nearly colourless prisms separate often $\frac{1}{8}$-inch in thickness. These are very soluble in water, even when cold, and also in alcohol; they appear, however, to be somewhat less soluble in water than the hydrochloride.

0·9210 gram of air-dry crystals lost at 100° 0·1045 gram .... = 11·35 per cent.
Calculated for $C_{12}H_{13}NO_3,HBr,2H_2O$ .. = 10·71 „
0·8165 gram of dry salt gave 0·5085 AgBr Br = 25·50 „
Calculated for $C_{12}H_{13}NO_3,HBr$ .... = 26·67 „

It was not found practicable to prepare dibromhydrocotarnine hydrobromide wholly free from tribromhydrocotarnine hydrobromide; the yellow crystalline mass obtained by adding bromine water in small quantities at a time and with continual agitation to a moderately-concentrated cotarnine hydrobromide solution until no further precipitate was produced, washing and drying over sulphuric acid, gave numbers agreeing approximately with those required for dibromhydrocotarnine hydrobromide, but indicating an admixture of about 15 per cent. of tribromhydrocotarnine hydrobromide.

0·5005 gram gave 0·5425 Cl_2 and 0·1380 H_2O.
0·6130 „ 0·7610 AgBr.

	Calculated for $C_{12}H_{13}Br_2NO_3,HBr$.	Calculated for $5C_{12}H_{13}Br_2NO_3,HBr +$ $C_{12}H_{12}Br_3NO_3,HBr$.	Found.
Carbon........	31·30	30·43	29·56
Hydrogen	3·05	2·92	3·06
Bromine	52·17	53·54	53·07

Another specimen, prepared with a more dilute solution of cotarnine hydrobromide, indicated a larger admixture of tribromhydrocotarnine hydrobromide, the numbers obtained indicating a mixture of about equal quantities of di- and tribromhydrocotarnine hydrobromide.

	Calculated.	Found.
Carbon	29·00	28·30
Hydrogen	2·73	3·14
Bromine..............	55·77	54·80

Whilst another specimen, made from a more dilute (about 1 per cent.) solution of cotarnine hydrobromide, consisted almost wholly, if not entirely, of tribromhydrocotarnine hydrobromide.

(A.) 0·3655 gram gave 0·3530 CO_2 and 0·083 H_2O.

Similarly, if cotarnine hydrobromide solution be poured into excess of bromine water, the precipitate consists, as might be expected, almost wholly of tribromhydrocotarnine hydrobromide.

(B.) 0·4560 gram gave 0·4360 CO_2 and 0·1030 H_2O.
0·3235 „ 0·4440 AgBr.

	Calculated.		Found.	
			A.	B.
C_{12}..............	144	26·71	26·34	26·08
H_{13}	13	2·41	2·52	2·51
Br_4.............	320	59·37	—	58·40
N	14	2·60	—	—
O_3..............	48	8·91	—	—
$C_{12}H_{12}Br_3NO_3,HBr$	539	100·00		

The tribromhydrocotarnine hydrobromide thus produced not only resembled that previously described in all respects, but also on heating to 190—200° it fused, evolving methyl bromide, and forming bromotarconine hydrobromide (§ 4 B). From this the free base was obtained, in the characteristic scarlet-orange hydrated crystals, becoming crimson on drying at 100°. The platinum salt gave these numbers—

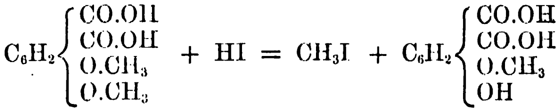
0·5615 gram gave 0·1115 Pt .... = 19·86 per cent.
Calculated for $(C_{11}H_8BrNO_3,HCl)_2PtCl_4$ = 20·23 „

The first-described product (chiefly dibromhydrocotarnine hydrobromide) on boiling with water gave a solution from which bromocotarnine hydrobromide was readily obtained in crystals on standing over sulphuric acid; but little non-crystalline bye-products were thus formed. The platinum salt gave these numbers—

0·7720 gram gave 0·1525 Pt .... = 19·75 per cent.
Calculated for $(C_{12}H_{12}BrNO_3,HCl)_2PtCl_4$ = 19·60 „

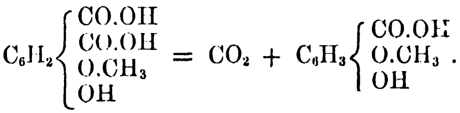
§ 6. *Noropianic Acid.*

It has been shown in Part III that when hemipinic acid is treated with strong hydriodic or hydrochloric acid solution at a nearly boiling temperature, the first action consists in the elimination of one methyl group, forming methyl norhemipinic acid, thus—



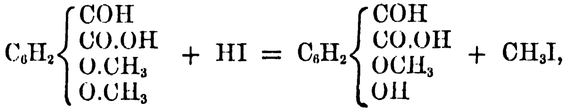
$$C_6H_2\left\{\begin{array}{l}CO.OH\\CO.OH\\O.CH_3\\O.CH_3\end{array}\right. + HI = CH_3I + C_6H_2\left\{\begin{array}{l}CO.OH\\CO.OH\\O.CH_3\\OH\end{array}\right.$$

and that this body then readily splits up, evolving carbon dioxide, and forming methyl protocatechuic acid, thus—



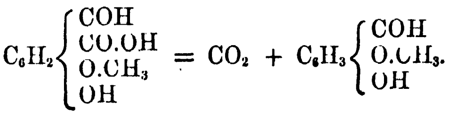
$$C_6H_2\left\{\begin{array}{l}CO.OH\\CO.OH\\O.CH_3\\OH\end{array}\right. = CO_2 + C_6H_3\left\{\begin{array}{l}CO.OH\\O.CH_3\\OH\end{array}\right. .$$

As Matthiessen and Foster have shown that the first action of hydriodic acid on opianic acid is represented by an equation parallel to the first one above, methyl noropianic acid being formed, thus—



$$C_6H_2\left\{\begin{array}{l}COH\\CO.OH\\O.CH_3\\O.CH_3\end{array}\right. + HI = C_6H_2\left\{\begin{array}{l}COH\\CO.OH\\OCH_3\\OH\end{array}\right. + CH_3I,$$

it seems not improbable that by the action of heat on this body vanillin or an isomeride might result by the further elimination of carbon dioxide—



$$C_6H_2\left\{\begin{array}{l}COH\\CO.OH\\O.CH_3\\OH\end{array}\right. = CO_2 + C_6H_3\left\{\begin{array}{l}COH\\O.CH_3.\\OH\end{array}\right.$$

The conditions requisite to produce this change, however, have not been found as yet. By continuing the action of heated hydriodic acid, however, the second methyl group becomes eliminated, and a new acid, the *noropianic acid* predicted by Matthiessen and Foster, is formed, though in quantity considerably below the theoretical amount, owing to its ready decomposibility, the reaction being—

$$C_6H_2\left\{\begin{array}{l}COH\\ CO.OH\\ OCH_3\\ O.CH_3\end{array}\right. + 2HI = 2CH_3I + C_6H_2\left\{\begin{array}{l}COH\\ CO.OH\\ OH\\ OH\end{array}\right. .$$

25 grams of opianic acid were heated to gentle ebullition with twice their weight of 50 per cent. hydriodic acid; in a few minutes about 24 grams of methyl iodide had distilled over, but the action then almost ceased, owing to the hydriodic acid becoming almost exhausted. On adding 50 grams more acid and continuing the heating, more methyl iodide passed over, the total amount collected being almost exactly 30 grams, or 120 per cent. of the opianic acid employed, the theoretical quantity for the above equations being 33·8 grams, or 135 per cent. The opianic acid employed must have been almost wholly converted, since some methyl iodide must of necessity have been lost in the process by imperfect condensation.

The residue left was largely diluted with water, and gently boiled with freshly precipitated well washed mercuric oxide. The filtered liquid deposited on cooling a small amount of a crystalline white substance very sparingly soluble in hot water, but readily dissolved by alkalies, and reprecipitated from the solution therein by acids. This substance gave no colour reaction with ferric chloride; the quantity was unfortunately insufficient for analysis. The filtrate from this contained an organic acid, which gave a deep bluish-green coloration with ferric chloride, and a copious canary-yellow precipitate with lead acetate (the liquid being free from all trace of iodine). This precipitate was washed and decomposed by sulphuretted hydrogen; on evaporation to a small bulk, the filtered liquid gave crystals not unlike those of opianic acid, but more soluble in water. These crystals were drained by the filter-pump, and twice recrystallised from water; when air-dry they yielded numbers agreeing with the formula of noropianic acid, $C_8H_6O_5,1\frac{1}{2}H_2O$. On drying at 100° a slight decomposition takes place, the crystals becoming slightly fritted together, and acquiring a greenish-grey shade.

A. 0·3330 gram dried at 100° lost 0·0470 gram.

B. 0·3135 of air-dry crystals gave 0·5285 CO_2 and 0·1320 H_2O.

C. 0·2895 gram lost at 100° 0·040 gram, and the residue gave 0·4865 CO_2 and 0·088 H_2O: total H_2O = 0·1280.

	Calculated.		Found.	
			B.	C.
C_8	96	45·93	45·97	45·83
H_9	9	4·31	4·68	4·91
$O_{6\frac{1}{2}}$	104	49·76	—	—
$C_8H_6O_5,1\frac{1}{2}H_2O$ ..	209	100·00	—	—

Loss at 100° :—A .... 14·11 per cent.
C .... 13·82 „
Calculated for $C_8H_6O_5,1\frac{1}{2}H_2O$ .... 12·92 „

When heated in a capillary tube after drying at 100°, noropianic acid first melts completely at 171° (cor.), the particles beginning to frit together a few degrees below; the fused mass solidifies to crystals on cooling. With ferric chloride it strikes a deep bluish-green, becoming brownish-red on further addition of ammonia or of sodium carbonate. It reduces silver nitrate on boiling only extremely slightly, but instantaneously reduces ammoniacal silver nitrate in the cold. In alkalies it dissolves with a brown or yellow coloration; the ammoniacal solution when evaporated to dryness leaves a residue insoluble in water like opiammone. Lead acetate throws down a voluminous *canary-yellow* precipitate.

From protocatechuic acid, which in some respects it resembles, noropianic acid differs in the coloration with ferric chloride (protocatechuic acid gives a brighter green, becoming blood red with ammonia or sodium carbonate), in giving a yellow lead salt instead of a white one, in the amount of water of crystallisation, in giving an insoluble residue when its ammonia salt is evaporated, and in its being less soluble in water.

Within the last few weeks Tiemann and Mendelssohn have described (*Deut. Chem. Ges. Ber.*, x, 393) a body isomeric with noropianic acid, and termed by them *isonoropianic acid*, or aldehydo-protocatechuic acid. Since this body is derived from aldehydo-vanillic acid (isomethyl noropianic acid) by demethylisation, it should *a priori* be not identical with the noropianic acid above described, inasmuch as opianic acid and the tetra-substituted benzenes thence derived appear, from the results obtained in the former parts of these researches, to contain the COH and CO.OH lateral chains in the ortho position with reference to one another, whilst the vanillic acid derivatives synthesized by the action of chloroform, appear to contain these chains in the meta position with respect to each other. In fact noropianic acid melts at 171°, and isonoropianic acid at 240°. Noropianic acid also differs from the quercimeric acid, $C_8H_6O_5$, of Hlasiwetz in the colours produced on addition of alkalis and ferric chloride, the latter giving with these reagents purple-red and deep blue respectively.

XXV.—*Note on Otto of Limes.*

By CHARLES H. PIESSE, Public Analyst for the Strand District (London), and C. R. ALDER WRIGHT, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School.

THIS oil is obtained from the rind of the fruit of the *Citrus limetta*, in the same way as the kindred ottos of orange and lemon, viz., by rasping the unripe fruits by rubbing them over a perforated concave metal rasp fixed over a basin. The pulp thus obtained is squeezed in a press and the otto which exudes purified by filtration; in this state it has the peculiar sweet sharp odour characteristic of the fruit. Ottos thus obtained are commercially more valuable than essential oils prepared by distillation from the same fruits, or from the residues left in this operation, having a more delicate perfume.

The specific gravity of the oil examined was found to be 0·90516 at 15·5°; when subjected to distillation a slight sputtering occurred due to the presence of a minute quantity of water; distillation commenced at 181°, and between this temperature and 186° about 70 per cent. of the oil passed over; only a minute quantity distilled between 186° and 250°, the residue, constituting a dark-brown gluey mass, giving indications of decomposition at higher temperatures; when cold it was a thick viscid soft resin, almost solid in consistency; after standing in the retort for three or four months a crystalline body began to appear in the midst of the resin and increased in amount for some two or three weeks; by the aid of the pump-filter these crystals were separated, with some difficulty, from the thick colophene-like matter; they were washed with some of the lowest distillate (181—186°), in which they dissolved but sparingly, and finally with a little alcohol of 90 per cent., in which they dissolved to some extent when cold, readily on boiling. The approximately pure crystals were straw-yellow and almost scentless; after crystallisation from boiling 90 per cent. alcohol and then twice from about 45 per cent. alcohol (equal volumes of strong alcohol and water), they were nearly white micaceous plates, quite destitute of odour, and melting at 162° (corrected). On combustion the following numbers were obtained agreeing best with the formula $C_{24}H_{28}O_5$:—

0·2050 gram gave 0·5480 CO_2 and 0·1360 H_2O

0·2290 ,, 0·6105 CO_2 ,, 0·1480 H_2O

	Calculated.		Found.	
C_{24}..........	288	72·73	72·91	72·71
H_{28}..........	28	7·07	7·37	7·18
O_5..........	80	20·20	—	—
	396	100·00		

Hence the body was not the hesperidin of Ed. Hoffmann (*Deut. Chem. Ges. Ber.*, 1876, 685), $C_{22}H_{26}O_{12}$, melting at near 245°; on fusion with potash at about 230° it yielded no protocatechuic acid. Its alcoholic solution was perfectly neutral; in water it was insoluble, but in caustic potash solution it dissolved to a lemon-yellow fluid from which acids precipitated white micaceous crystals. On gently heating over the melting point it charred and gave off inflammable vapours, but could neither be distilled not sublimed with decomposition.

The distillate below 186° was faintly yellow; on redistillation about 99 per cent. passed over almost constantly at 176°, a little of a colourless fluid exhibiting no constant boiling point, distilling between 180° and 230°, and only a minute quantity of resinous matter being then left in the distilling vessel. The boiling point of the main fraction was not sensibly altered by cohobation with sodium; hydrogen was, however, evolved during the process and a reddish flocculent substance separated which was not further examined. The distillate obtained after this treatment gave numbers showing that it was a hydrocarbon of the terpene family—

0·173 gram gave 0·558 CO_2 and 0·187 H_2O

	Calculated.		Found.
C_{10}	120	88·23	87·96
H_{16}	16	11·77	12·01
$C_{10}H_{16}$..........	136	100·00	

Hence otto of limes consists of a soft resin, not volatile at 250°, dissolved in somewhat more than twice its weight of a terpene boiling at 176° (uncorrected).

The terpene of orange oil (boiling at 178°) has been shown by one of us (this *Journal*, 1873, 686) to yield cymene readily by treatment with bromine in proportion to realize the equation—

$$C_{10}H_{16} + Br_2 = 2HBr + C_{10}H_{14},$$

the bromine being cautiously added to the terpene and the resulting dibromide, $C_{10}H_{16}Br_2$, being then heated in a flask with an inverted condenser attached. On the other hand, Oppenheim found (*Deut. Chem. Ges. Ber.*, v, 628) that citrene, the terpene of lemon oil boiling at 173—174°, and turpentine terpene boiling at 160—161°, do not yield cymene in any quantity by this mode of treatment, although they form about 30 per cent. of the calculated amount on heating with aniline in sealed tubes. An analogous result was also obtained by one of us (*loc. cit.*) with the terpene of nutmeg oil, myristicene, boiling at 163—164°. In order to see whether the ease with which the dibromides $C_{10}H_{16}Br_2$ split up on heating into hydrobromic acid and cymene is connected with the boiling points of the terpenes, the lime terpene was converted into dibromide by cautious addition of the calculated amount of bromine. On heating the product torrents of hydrobromic acid escaped; the majority of the substance, however, was converted into a black pitch-like mass, but little cymene being formed. After heating until the evolution of hydrobromic acid nearly ceased, the substance was distilled and the small amount of distillate obtained purified by cohobation with sodium and finally by treatment with concentrated sulphuric acid and dilution with water; the oily layer which thus separated was again distilled over sodium; a hydrocarbon passed almost absolutely constantly at 176° and appeared to be cymene, but contaminated with a minute amount of some brominated compound (probably $C_{10}H_{15}Br$) which had resisted all the attempts at purification—

I. 0·2335 gram gave 0·746 CO_2 and 0·2275 H_2O
II. 0·309 „ 0·989 CO_2 „ 0·304 H_2O

	Calculated.		Found.	
C_{10}	120	89·55	87·13	87·28
H_{14}............	14	10·45	10·82	10·93
$C_{10}H_{14}$	134	100·00		

The yield of this hydrocarbon was not more than 10—15 per cent. of the terpene employed, whence it would seem that, notwithstanding the nearness of the boiling point of the lime terpene to that of hesperidene the two terpenes are very dissimilar, since hesperidene readily yields upwards of 80 per cent. of pure cymene by this mode of treatment. From the boiling point of the lime terpene and its behaviour in this respect it seems highly probable that it is identical with citrene, the terpene of the lemon.

The identity of the cymene prepared as above with ordinary cymene was established by oxidizing it with a mixture of sulphuric acid, water, and potassium dichromate; terephthalic and acetic acids were thus produced.

No. XXVI.—*On the Action, at a High Temperature, of Volatile Metallic Chlorides on Certain Hydrocarbons.*

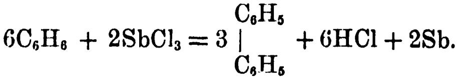
By WATSON SMITH.

Part I. IN the preparation of isodinaphthyl by passing the vapour of naphthalin through a red hot tube, the yield is but small, and hence, to obtain a considerable quantity, many distillations of the same substance have to be made, the small residue of high boiling product after each distillation being poured out, and kept apart. Wishing to have a more convenient method, so as to prepare large quantities of the isodinaphthyl, if necessary, I made this matter a subject of investigation.

In my first paper, giving an account of the discovery of isodinaphthyl (*Proc. of Literary and Phil. Soc.*, Manchester, 1871), I mentioned an experiment, in which chlorine together with naphthalene vapour, was passed through a red hot tube. *Complete* decomposition appeared to take place, dense volumes of black smoke emerging at the end of the tube. However, it seemed likely on further consideration, that if, instead of free chlorine, a metallic chloride were used, yielding at a high temperature its chlorine at least in part, a *partial* decomposition only might be effected. Accordingly, antimony trichloride and tin tetrachloride were chosen as suitable chlorinating agents. After passing naphthalene and antimony trichloride vapours through a red hot tube, and succeeding in realising the increased yield of isodinaphthyl, I turned my attention to benzene and toluene, in the hope of making the method a general one, and obtaining diphenyl and stilbene. The results I now give under their respective headings :—

BENZENE.

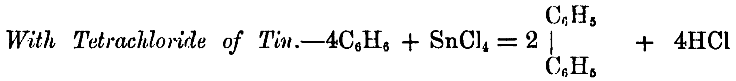
With Antimony Trichloride.—The reaction expected is represented in the following equation :



$$6C_6H_6 + 2SbCl_3 = 3\begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array} + 6HCl + 2Sb.$$

Accordingly, equal weights of trichloride and benzene were taken. The benzene was placed in a flask connected with the flask containing the antimony trichloride by a bent tube, and the trichloride flask with a tube of hard Bohemian glass placed in a gas combustion furnace, by means of another bent tube. Thus, the vapours from the boiling benzene were passed through the flask containing the boiling antimony trichloride, the mixed vapours passing through the combustion-tube, which was filled loosely with bits of pumice-stone and porcelain. The receiver of the apparatus was connected with a Liebig's condenser, to condense undecomposed benzene.

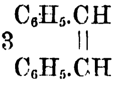
On distilling through the tube, at a bright red heat, large volumes of hydrochloric acid were given off, and metallic antimony deposited plentifully, at the extremity of the tube, and in the neck of the receiver. After all had passed through, the contents of the receivers (the one at the end of the tube, and that connected with the Liebig's condenser) were returned to the benzene flask, a fresh quantity of trichloride added in the other flask, and the distillation repeated. A high-boiling residue being left, this was poured out at the end of the second distillation, and kept apart. Three distillations were made. The accumulated residues of these three distillations, consisting of a mixture of diphenyl with excess of undecomposed antimony trichloride, metallic antimony powder, and a little benzene, were placed in a small retort and distilled. A little benzene came over, then from 200° to 220° much antimony trichloride, and finally above 220°, a mixture containing diphenyl with less trichloride. The latter was treated with warm concentrated hydrochloric acid, the trichloride being dissolved, and diphenyl left floating as an oil in the warm acid solution. On cooling, the solid cake was removed, again washed with acid, and recrystallised from alcohol. *The melting point was exactly* 70°, *the boiling point* 243° C. Thus a considerably increased yield of diphenyl was obtained, over what is obtainable by the red-hot tube alone, but the quantity still not being great enough, I determined to try the effect of tetrachloride of tin in a similarly conducted experiment.



With Tetrachloride of Tin.—$4C_6H_6 + SnCl_4 = 2 \begin{array}{c} C_6H_5 \\ | \\ C_6H_5 \end{array} + 4HCl$ + Sn represents the reaction expected. 62·4 grams of benzene were distilled through the red-hot tube, as in the former experiment, together with 52 grams of tin tetrachloride, the benzene vapours being passed through the flask containing the *tetrachloride of tin.* The mixed gases came over of a dusky or grey colour, a small quantity of a violet-coloured oil being deposited in minute drops in the neck of the receiver. This violet oil was noticed also in the former experiment with antimony trichloride. The evolution of hydrochloric acid gas was very large, much larger than in the former experiment, and towards the end of the distillation the tubes were stopped up with a mixture of diphenyl and stannous chloride; also in the receiver cakes of diphenyl with stannous chloride were found. Much metallic tin was also found in the receiver. This one distillation thus gave a very large yield of diphenyl; further very little benzene came over through the Liebig's condenser, showing that the decomposition was almost complete. This method therefore appears to be the simplest, quickest and best for procuring diphenyl in large quantity from benzene. The above equation does not, however, appear to give an exact representation of the reaction in the tube; this reaction seems indeed to be a mixed one, stannous chloride and metallic tin being reduced. This is probably owing to want of uniform mixture in the tube.

TOLUENE.

With Antimony Trichloride.—Reaction expected: $6C_7H_8 + 4SbCl_3 =$

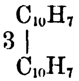


$$3\begin{array}{c}C_6H_5.CH\\ \|\\ C_6H_5.CH\end{array} + 12HCl + 2Sb_2.$$

About 60 grams of toluene were taken, and distilled so that the vapours passed into a flask containing boiling antimony trichloride, the mixed vapours then passing through the red-hot tube. Large volumes of hydrochloric acid were evolved, and much metallic antimony reduced. When all was passed through, the contents of the receiver were placed in a small retort, the toluene was distilled off and replaced in the first flask, the residue, containing much undecomposed trichloride, being returned to the second flask. The distillation was then repeated. Hydrochloric acid was again abundantly evolved. The contents of the receiver, together with the residue in the second flask, were now distilled to remove toluene and antimony trichloride; a residue remained which was treated repeatedly with hot concentrated hydrochloric acid to remove antimony trichloride. An oily black mass remained floating on the hydrochloric solution. On distilling this tarry substance the temperature rapidly rose to 270°, when a small quantity of a red oil came over, having a strong, rank, disagreeable odour, resembling that of burnt cheese. From 280° to 300° an oil came over with a still more disagreeable odour. Above 320° a thick gummy oil distilled over, but mostly remained condensed in the stem of the retort, and crystallised there in long striated masses of crystals.

NAPHTHALENE.

With Antimony Trichloride through the Red-hot Tube.—$6C_{10}H_8 +$



$$2SbCl_3 = 3\begin{array}{c}C_{10}H_7\\ |\\ C_{10}H_7\end{array} + 6HCl + Sb_2.$$

—77 grams of naphthalene and 46 grams of antimony trichloride were mixed together by fusion in the same flask, and then distilled through the red-hot tube. This tube was, as in the previously described experiments, of hard Bohemian glass, and was nearly double the diameter of the ordinary combustion tubing. The boiling point of the trichloride being nearly that of naphthalene, there is no difficulty in thus distilling them together. The results were as follow:—

1*st Distillation.*—Tube at a bright red heat. Much hydrochloric acid evolved, and metallic antimony reduced.

2nd Distillation.—After all had passed through, the still fused contents of the receiver were returned to the distillation flask, and again passed through, 15 to 16 grams of trichloride being further added. More hydrochloric acid appeared to be evolved than in the first distillation, and antimony was abundantly deposited. The temperature was however, a little higher than in the first distillation, being a full bright red heat. A large residue was obtained of high-boiling product in the distillation flask. There is no difficulty whatever in recognising the point at which the naphthalene and trichloride have all passed over, as the residue, consisting chiefly of isodinaphthyl, boils at a very high temperature, and therefore ebullition ceases unless the lamp flame be turned further on.

3rd Distillation—No more antimony trichloride was added, but another distillation was made. Tube at a bright red heat. Residue obtained was somewhat larger than in the second distillation. Yellow vapours came over in some abundance.

4th Distillation.—Added no more trichloride, that remaining undecomposed sufficing. Residue as large as ever, of high boiling product. Of course the last distillation only yields a residue, which it leaves behind it, and hence the product is one of three distillations.

The collected crude black looking product weighed 37·4 grams.

This black mass was now distilled in a small retort, when a yellow, hard, crystalline mass was obtained, consisting of crude isodinaphthyl. In this distillation, after the isodinaphthyl had for the most part passed over, a quantity of a yellow sublimate came over with the latter portions, and this, with the final portions, gave place to a red sublimate. This red sublimate sometimes appeared as the pitchy residue became coked, the retort bottom being red-hot. These sublimates I intend to examine further.

Of the crude yellow crystalline isodinaphthyl, the weight was 24·2 grams. This amounts to 31·4 per cent. on the naphthalene taken, whilst the crude black substance = 48·5 per cent. on the naphthalene taken.

A comparison will show the wonderfully increased yield of substance by this method over that in which naphthalene was distilled alone through the tube:—

(*a.*) *Naphthalene alone used.*—After eight distillations through the red-hot tube: crude black substance.............................. = 17·23 per cent.

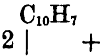
(*b.*) *Naphthalene with Antimony Chloride.*—After three distillations through the red-hot tube: crude black substance .... = 48·5 „

After redistilling (*b*) to purify it partially: yellow crystalline redistilled substance .... = 31·4 per cent.

A singular fact is here well worthy of notice, viz., the product obtained as above described was much purer than any previously obtained by using naphthalene alone, or a smaller quantity of antimony trichloride than the theoretical, or some excess over it. The increased purity was well observed in purifying two samples by triturating about the same weights of each with petroleum spirit, and filtering. One sample had been prepared at the same temperature as the other, but in the one case about half the equivalent weight of trichloride had been used, in the other the full amount.

With the first-named product much less yellow sublimate was yielded, and scarcely any red sublimate, on coking. The petroleum spirit solution had merely an orange colour. In the case of the other, a large yellow sublimate was obtained. A considerable quantity of a fine orange and red on coking, and an almost blood-red solution was obtained in the filtrate, on washing with petroleum spirit. A product nearly as much contaminated with this yellow decomposition-product has been frequently obtained with naphthalene alone. From the red petroleum spirit wash-liquors, a substance gradually separates out in small crystalline clusters of a citron-yellow colour. A sufficient quantity having now been obtained for the first time for working upon, I have been enabled to examine it. It will be described further on, with the results obtained on making a minute examination of the red petroleum spirit mother-liquors referred to.

With Tin Tetrachloride.—Expected reaction: $SnCl_4 + 4C_{10}H_8 =$



$2\begin{array}{l}C_{10}H_7\\ | \\ C_{10}H_7\end{array} + 4HCl + Sn$, and $2SnCl_4 + 4C_{10}H_8 = C_{20}H_{14} + 4HCl + 2SnCl_2$. 79 grams of naphthalene, and 40 or a little over of tetrachloride, were taken. The first time the distillation was attempted, with apparatus similar to that previously employed, the tubes and pipe soon became stopped up, so that it was impossible to proceed. This was owing to the considerable complete decomposition which was going on in the tube, carbon being separated; this either accumulated in the main tube and caused stoppage there, or was carried in fine dust, together with stannous chloride into the other tubes of the apparatus. Another apparatus had therefore to be devised in which an empty tube was used, and only wide-necked bottles and tubing for the receiver and apparatus for condensing the hydrochloric acid. The latter consisted simply of a wide-necked bottle loosely filled with blotting-paper soaked in water, and containing a little water at the bottom. On distilling, it was at once noticed that a considerable amount of black smoke was formed, and issued at the end of the tube, also very much hydrochloric acid vapours. The tube was nearly white hot. After the experiment the tube was found to be full of shining black scales of separated carbon, and the stuff which had distilled over into the receiver was quite black, but more fluid, or rather soft, than even before. This mass was transferred to a small retort and distilled. First some naphthalene came over, then what were evidently chlorine-products of naphthalene; the temperature then rose rapidly from 220° to 300°, when a small quantity of a reddish-yellow oil came over which partially crystallised on cooling. It exactly resembled some of those oils known as the "red anthracene oils," well known to tar-distillers. This oil is quite a new feature, and will be examined more minutely at the earliest opportunity. Next in order of distillation, the isodinaphthyl came over, looking exactly as usual, and behaving so to all tests. Lastly, an unusually large quantity of the citron-yellow powder distilled, or rather sublimed over, and dropped out at the end of the retort, forming a little heap of yellow powder quite separate from the isodinaphthyl, which remained solidified in the stem of the retort. A large yield of isodinaphthyl was obtained, but the method is not so convenient as when antimony trichloride is used. I propose, however, to try the effect of heating naphthalene to a high temperature with tin tetrachloride in sealed tubes, when I hope to avoid the total decomposition and get a larger yield of isodinaphthyl.

It was found on purifying the crude isodinaphthyl, that on crushing the crude yellow substance obtained by the distillation of the black residues of the first operation, an odour like that of phenol was observed. This being the case, the whole quantity of substance was boiled with dilute sodium hydrate solution and filtered, and then the filtrate was decomposed by dilute sulphuric acid, when an oily, semi-solid, floccular mass rose to the surface, having a strong odour like that of phenol. This is probably naphthol, formed by the action of small quantities of water in the antimonious chloride used upon the naphthalene in the red-hot tubes.

It is interesting to notice the great stability of *benzene* in the red-hot tube with the chlorides mentioned, in comparison with naphthalene, apparently little else being formed than diphenyl, and scarcely any black smoke or separation of carbon being perceived. In the case of naphthalene, on the contrary, under these circumstances much carbon is separated; in fact the tube, though an empty one, becomes almost choked: also a considerable quantity of other decomposition-products is formed. Toluene appears to suffer considerable dismemberment, yet but little carbon is separated.

II. *Isodinaphthyl Sulpho-acids and Salts, with certain other derivatives.*—Merz and Ebert (*Deut. Chem. Ges. Ber.*, viii, 1876, 592) found that a mixture of concentrated sulphuric acid and naphthalene in the proportions of 5 : 1, heated for a long time at 100°, gave only mixtures of isomeric monosulpho-acids, together with a certain quantity of the isomeric disulpho-acids. Also it was found impossible to prepare the α-mono- or di-sulpho- acids uncontaminated with some of the respective β-sulpho-acids.

A mixture of naphthalene and concentrated sulphuric acid in the proportions of 1 to 3, heated for about eight hours from 140° to 160°, yielded a considerable amount of β-mono-sulpho-acid. After 14 hours' heating much β-disulpho-acid was found to have formed.

1 part of naphthalene with 5 parts of concentrated acid heated for four hours to 160°, yielded nearly equal quantities of α- and β-disulpo-acids. No mono-sulpho-acids were formed.

Naphthalene and acid in proportion of 1 to 5, heated 24 hours to 180°, yielded the β-disulpho-acid with only a trace of the α-isomeride. The α-derivatives were more fusible and more soluble than the β-isomerides. It was found that iso-dinaphthyl dissolves easily in concentrated sulphuric acid at a temperature of from 140° to 150°. In the first experiment a considerable excess of concentrated sulphuric acid was used, and the iso-dinaphthyl being added, the whole was heated in the oil-bath from 140° to 150° for three or four hours. Afterwards the black viscous liquid was dissolved in water, and excess of barium carbonate added; to another portion also excess of lead carbonate was added. After filtering, and washing with hot water in each case respectively, the solutions were evaporated, when in both cases a white precipitate of a slightly crystalline appearance fell. This turned out to be difficultly soluble β-barium or lead sulpho-salt. On filtering, and evaporating on the water-bath, and finally over sulphuric acid, glassy masses were obtained, of which the barium compound easily split up into small lance-shaped plates. These residues were very soluble in water, and were found to be the isomeric α-barium and lead salts. In the present case a large yield of the α-soluble salts was obtained. The barium α-salt was a mass composed of little transparent lance-shaped plates of a light brownish colour. The lead α-salt was a light yellow, scaly mass. About 4 parts of isodinaphthyl were mixed in a small flask with 2 parts of concentrated sulphuric acid, and the whole was heated to between 180° and 190° for five hours. On cooling, a black shining solid mass was obtained with a green lustre. It dissolved completely and easily in water. On neutralising with barium carbonate, filtering, and washing with hot water, a solution was obtained, which on evaporation yielded a large proportion of the β-salt as a pure white crystalline or scaly precipitate. A very small yield of the α-isomeric salt was obtained as a glassy, transparent, and very soluble mass on slowly evaporating the filtrate over sulphuric acid.

The *α-sulpho- acid* was obtained by treating the barium salt with sulphuric acid till no further precipitate was formed. On filtering and evaporating to dryness slowly and at a gentle heat, a residue was obtained consisting of little transparent scales which have a faint yellowish tint and are slightly fluorescent. The acid is easily soluble in water, slightly in absolute alcohol, freely soluble in spirits of wine and in ether, and is precipitated from the ethereal solution by absolute alcohol. It is quite insoluble in benzene. The *β-sulpho-acid* was also prepared, and it closely resembles the α-acid, but is characterised by less solubility. The *α-lead salt* was found to be almost insoluble in ether, alcohol, and benzene. It is easily soluble in water and weak alcohol. The β-salt is almost insoluble in alcohol, ether, and benzene, but is only slightly soluble in water.

That the above-named acids are isomeric I have convinced myself by repeated analyses, but my numbers are not sufficiently concordant with theory to induce me to publish them. This may probably be due to the presence of some third body, or of impurities.

On triturating a quantity of the potassium salt of the sulpho-acids above-mentioned with phosphorus pentachloride, no action was perceptible; heat also did not appear to assist in the reaction; the endeavour to prepare a sulpho-chloride therefore failed.

An *oxydinaphthyl* or *phenol* was obtained as follows:—Equal parts by weight of the potassium salt of the sulpho-acid and potassium hydrate were mixed with a little water and the whole was gradually heated up to 250° in an atmosphere of hydrogen. The mass assumed a bright-yellow tint, gradually changing to brownish-yellow. On leaving it to cool and treating with hydrochloric acid, a soft resinous mass detached itself from the solution, which, when dry, thoroughly hardened on fusing to a solid, rich, brown resinous mass. This oxydinaphthyl possesses a faint but distinct phenol-like odour. It is very soluble in alcohol, less so in ether, slightly in benzene. It dissolves readily in a solution of an alkaline hydrate, from which solution acids separate it as a thick jelly-like resinous mass with a faint phenol-like odour.

Nitro-substitution Product.— On dissolving isodinaphthyl in nitric acid and pouring the solution into water, a white precipitate is thrown down, consisting of a nitro-compound. On heating the well-dried precipitate gently, it fuses, and on cooling again forms a reddish-brown transparent resin. The substance altogether very much resembles in appearance and properties the nitro-compound obtained by Lossen from his dinaphthyl. The body is but little soluble in alcohol, almost insoluble in ether, freely soluble in benzene. The benzene solution on evaporation left it as a yellow resin. It was reduced on treatment with tin-foil and hydrochloric acid, but the quantity of amido-derivative formed was too small for examination.

Cyanogen-derivative.—On distilling equivalent proportions of the potassium salt of the sulpho-acid and potassium cyanide, both being perfectly dry, a distillate was obtained crystallising in the stem of the retort in beautiful long white needles. The amount obtained was too small for analysis.

III. *A new Dinaphthyl and a consideration of the Positions of the three Isomeric Dinaphthyls.*—I have already drawn attention to the fact that, together with isodinaphthyl, a yellow substance soluble in petroleum spirit is formed when naphthalene is submitted to the action of a high temperature, either alone or in presence of easily decomposible and volatile metallic chlorides. In the latter case, more of this yellow substance is formed, the more easily decomposible the metallic chloride used is. Thus, more is obtained when tin tetrachloride is used than when antimony trichloride is. In purifying the crude isodinaphthyl by crushing and triturating with petroleum spirit a fine red solution is obtained on filtering. This red solution was evaporated down to a certain extent and then set aside to evaporate spontaneously. After the lapse of a week or two, wart-like crystalline masses were deposited in considerable quantity. The mother-liquors were poured off these and again allowed to stand and deposit another crop of crystals. The accumulated stock of crystals was at length taken and pressed between blotting-paper, then ground up finely to a thin paste with a little petroleum spirit, and again pressed between blotting-paper. A yellow powder was thus obtained, fusing at a low temperature, and dissolving in warm concentrated sulphuric acid, to which it communicates a fine violet tint.

This yellow powder was now placed in a retort and distilled. A very little oil came over first, which was rejected; the temperature then rose immediately to over 300°. At this high temperature almost all came over, and condensed as a thick, transparent, light yellow, resinous mass which only partially solidified. This mass remained clear for a week, when it began to show signs of crystallisation at the edges, which became white and opaque. The mass required a month to crystallise thoroughly. It is very soluble in petroleum spirit, ether, and benzene; less soluble in alcohol than in ether. Weak alcohol precipitates it from solution in absolute alcohol. A concentrated hot alcoholic solution deposits the body in resinous drops on cooling. If, however, dilute solutions of the body in petroleum spirit or benzene be allowed to evaporate slowly in the air, small tufted crystalline masses were obtained. On making very dilute solutions in petroleum spirit and letting these evaporate slowly in the air, it was noticed that the crystals first formed were tufted with little yellow plates, and here and there entirely composed of tufts of transparent light-yellow plates; the other crystals were simply the rough semiglobular wart-like masses before mentioned. On determining the melting points of these, it was found that the little plates melted at

137°, the warty masses at 75°. It was clear therefore that here were two different substances, and the next point was to separate and purify them. This was effected by a tedious process of fractional crystallisation, extending over several months. The body melting over 75° was very difficult to obtain well crystallised, and this point was only attained by taking a very dilute petroleum-spirit solution and allowing this to evaporate spontaneously in small flasks, these being set aside in a warm place. Small tufts of crystalline plates, intermixed with a few of the warty masses, first crystallised out. The spirit was poured off these into another flask, and from the mass of crystals left the plate-like ones were picked out and set aside; this was done as long as any plates separated. When no more plates would crystallise out the warty or globular masses were redissolved, the solution was further diluted, and the whole again set aside. This time the crystals forming were almost white and of a pearly scale-like appearance, and it was noticed besides that a few thin plates of a brownish-red colour and transparent had crystallised out. This was evidently a new substance, but it existed in extremely small quantity, so that only a few crystals were obtained. The plates first mentioned were collected and recrystallised from petroleum spirit, in which they were considerably less soluble than the white pearly crystals. They were by repeated crystallisation obtained almost quite white, and had a constant melting point of 147°. This body resembled isodinaphthyl in appearance, but it differed from this hydrocarbon in melting point and in being more soluble in benzene, petroleum spirit, alcohol and ether, &c. Several careful comparisons were made as to the relative solubilities of the two bodies, which amply confirmed the belief that they are not identical. In fact the solubilities in various fluids, the appearance, and the not very far-removed melting point, led me to suspect this was no other than the isomeric dinaphthyl obtained by Lossen (*Liebig's Annalen*, lxviii, 71), by the action of manganese and sulphuric acid on naphthalene. The low-melting substance, after several crystallisations, melted constantly at 75°. Its boiling point was over 300° (as was also that of the body melting at 147°). It was far more soluble in petroleum spirit, benzene, alcohol, and ether than the higher melting substance, and crystallised out much more quickly from these solvents. The very small quantity of the body crystallising out in brown transparent plates was collected and tested. The *melting point* was found to lie between 250° and 255°. It was slightly soluble in petroleum spirit, less in alcohol, but rather more soluble in ether; it was still more soluble in boiling benzene, to which it communicated a splendid blue fluorescence. A very small crystal communicates a magnificent blue fluorescence to a very large bulk of benzene or alcohol in which it is dissolved. This body reminds one very much of the brown polymeric body obtained by (*Liebig's Annalen*, lxviii, 89) Lossen and (*ibid.*, cxlvii, 170) Otto, with which it is probably identical. It was only after very long standing (about a month) and slow evaporation that it was obtained crystallised. When more quickly separated it appears as a chocolate, brown powder. I believe it to be identical with the polymeric dinaphthyl above-mentioned, already obtained by other methods, by Lossen and Otto.

With respect to the body melting at 147°, which in properties seemed to resemble the dinaphthyl obtained by Lossen, it will be remembered that Otto (*Liebig's Annalen*, cxlvii, 170) obtained a body crystallising from alcohol in little yellow plates, and melting at 133°, by heating mercuro-dinaphthyl with soda lime. Now this body Otto seemed to think might possibly be identical with Lossen's dinaphthyl, as it agreed very well in its properties, excepting that the melting point was lower, 133°, Lossen's melting at 154°). Otto had extremely little substance, and this appeared to be not quite pure, "of a canary-yellow colour." Now the substance I obtained agrees exactly in all respects with that described by Otto, appearing first in little canary-yellow plates melting at 137°, and dissolving in alcohol, ether, benzene, and petroleum spirit. By carefully recrystallising, however, the body was obtained almost white, and then it melted at 147°. I do not think it at all impossible that the dinaphthyl obtained by Lossen may have been mixed with traces of the isodinaphthyl melting at 184°, and formed in small quantity by Lossen's process simultaneously with his hydrocarbon. Such an event would readily account for a melting point being raised 7° (*e.g.*, 147° to 154°). On the other hand, I cannot think that my hydrocarbon melting at 147° was perceptibly contaminated with the body melting at 75°, as the former crystallised out at once on cooling from alcohol, and so could easily be filtered and washed free from the latter, which never began to crystallise till after several days The body melting at 75°, and already described, I believe to be a third dinaphthyl, thus completing the number of possible isomerides of this hydrocarbon. Combustions were made of these two new bodies, with the following results:—

Substance melting at 147°.

Weight of substance taken ...... = 0·3295 gram.
Weight of CO_2 obtained .... = 1·1410 „
Weight of H_2O obtained .... = 0·1755 „

	Found.	Calculated for $C_{20}H_{14}$.
Carbon	94·44	94·48
Hydrogen	5·91	5·52
	100·35	100·00

Substance melting at 75°.

Weight of substance taken ...... = 0·3000 gram.
Weight of CO_2 obtained .... = 1·0420 „
Weight of H_2O obtained .... = 0·1550 „

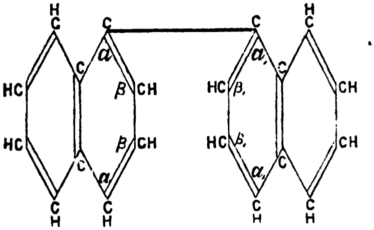
	Found.	Calculated for $C_{20}H_{14}$.
Carbon	94·73	94·48
Hydrogen	5·74	5·52
	100·47	100·00

The combustions of this body were a matter of some difficulty, owing to the refractory nature of the substance, and I take this opportunity of thanking my friend Mr. T. G. Young for his assistance in the operations.

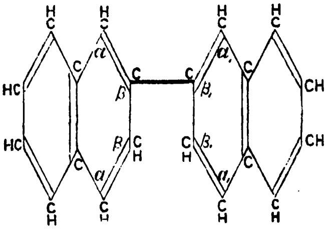
It would now appear that there exist three isomeric dinaphthyls, all of which are obtainable, though in very different quantities, by passing naphthalene, together with antimony chloride, through a red-hot tube. By far the largest proportion consists of isodinaphthyl, melting at 187°; the next in quantity is the low-melting isomeride (75°); the one melting at 147°, and apparently identical with Lossen's, is formed by this method in extremely small quantity. It is curious to notice the regular gradation in *solubility*, *crystallisability*, and *fusibility* in the case of these three isomerides.

Dinaphthyl No. 1 (Isodinaphthyl).	*Dinaphthyl* No. 2 (Lossen's).	*Dinaphthyl* No. 3.
Melting points 187°	147°. (Smith)...... 154°. (Lossen)	75°.
Crystallisability— Most readily crystallisable. Beautiful rhombic plates, very regular, and the prevailing crystalline form from solvents, even from very impure solutions.	Crystallises readily, but not so much so as No. 1. Crystallisability modified more by impurities present, and crystalline form more variable.	Very difficult to crystallise. Requires some days or a week. Crystalline form subject to considerable modification.
Solubility— Difficultly soluble in alcohol and ether. Benzol and petroleum spirit must be boiling to dissolve it freely, and also be in excess.	Soluble in alcohol and ether, &c., much more so than No. 1.	Very soluble in all the afore-named liquids, from which it crystallises with great difficulty.

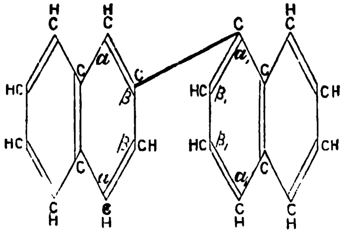
Practically there are three possible dinaphthyls, namely, the following:—



α-α-Dinaphthyl (Lossen's).



β-β-Dinaphthyl.



α-β-Dinaphthyl.

Undoubtedly Lossen's dinaphthyl must be the α-α-isomeride, as he obtained it by the action of sodium-amalgam on α-bromnaphthalene. With regard to the other two dinaphthyls, I consider it extremely probable that the so-called isodinaphthyl obtained by me, and melting at 187°, is the β-β-isomeride, and this view is supported by the following consideration:—Liebermann, in his "Studien in der Naphtalingruppe" (*Liebig's Annalen*, clxxxiii, 271; *J. Chem. Soc.*, April, 1877), on comparing the melting points of the corresponding isomeric α- and β-naphthalene derivatives, has observed that out of *fourteen* well studied and known bodies, *twelve* of those in the β-class melt higher than their isomerides in the α-class. The examples, which are very striking, are as follows:—

Isomeric Naphthalene Derivatives.

	Melting Points.			*Melting Points.*	
	α.	β.		α.	β.
$C_{10}H_7Cl$	liquid	56° (61, 53 ?)	$C_{10}H_7.NH_2$	50°	112°
$C_{10}H_7Br$	liquid	69°	$C_{10}H_7.NH.C_2H_3O$.	159°	132°
$C_{10}H_7Cy$	37°	66°	$C_{10}H_7.CO_2H$	161°	181°
$C_{10}H_7.OH$....	94°	122°	$C_{10}H_7.COCl$	liquid	43°
$C_{10}H_7.OC_2H_5$.	liquid	33°	$C_{10}H_7.CONH_2$....	204°	192°
$C_{10}H_7.OC_2H_3O$	liquid	60°	$C_{10}H_7.CO.C_6H_5$ ..	75°	82°
$C_{10}H_7.SH$....	liquid	137°	$C_{10}H_7.SO_2Cl$	66°	76°

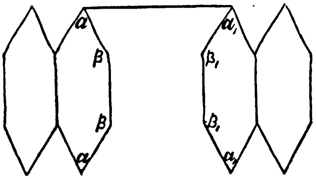
Now regarding these numbers so arranged, it may be observed that dinaphthyl, also a naphthalene derivative, most probably forms another example of the peculiarity noticed by Liebermann. Thus—

	α.	β.	α-β.
$C_{10}H_7.C_{10}H_7$....	154° (147°)	187°	75°

[illegible] er than the so-call[illegible] phthyl, a[illegible] y dinaphthyl in the α-β-p[illegible]

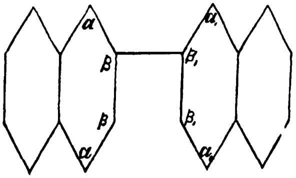
The balance of probability then appears to favour the following arrangement:—

α-α-Dinaphthyl (Lossen's).



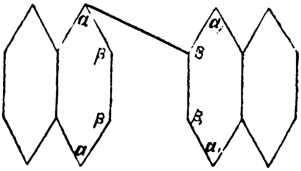
Melting point = 154° (147°).
Generally soluble; crystallises with moderate facility.

β-β-Dinaphthyl (Isodinaphthyl).



Melting point = 187°.
Not easily soluble; crystallises very readily.

α-β-Dinaphthyl.



Melting point = 75°.
Very soluble, and difficult to crystallise.

All the dinaphthyls boil above 300°, but that melting at 75° does not appear to boil so high as the one melting at 187°. Possibly the one melting at 147° has an intermediate boiling point.

It is probable that by gentle oxidation of these dinaphthyls, the corresponding isomeric naphthoic acids may be obtained, viz., from α-α-dinaphthyl one might expect to get α-naphthoic acid, from β-β-dinaphthyl β-naphthoic acid, whilst α-β-dinaphthyl would probably yield a mixture of these isomeric acids. It is further very possible that by the exhaustive chlorination of these hydrocarbons, much light may be thrown upon their respective isomeric constitutions. Ruoff in this manner obtained extremely interesting results with diphenyl, viz., the formation of perchlorodiphenyl. It would be interesting to ascertain whether by this action of chlorine, perchlorodiphenyl or perchlorobenzene could be formed from the dinaphthyls. A further examination of the respective sulpho-acids of these bodies, their conversion into the corresponding cyanides by distillation with potassium cyanide, and after-treatment with alcoholic potash, with possible formation of the isomeric naphthoic acids, would also probably yield much instruction. These further researches I intend to take up on an early occasion.

I conclude, thanking Prof. Lunge, in whose laboratory this work was done, for his kindness to me whilst thus engaged.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Thermo-chemical Researches. By JULIUS THOMSEN (*J. pr. Chem.* [2], xv, 435—473).—*Platinum and Palladium.*—The following tables give the results obtained:—

(*a.*) *Heat of Formation of the Haloïd Double Salts of Platinum.*

Reaction.	Heat evolved.	Explanation.
$Pt,Cl_4,2KCl$	89,500 units	Anhydrous salts corresponding with the chloride and bromide.
$Pt,Br_4,2KBr$	59,260 „	
$Pt,Cl_4,2NaCl$	73,720	
$Pt,Br_4,2NaBr$	46,790	
$Pt,Cl_4,2NaCl,6H_2O$	92,890	Hydrated sodium-platinum chloride and bromide.
$Pt,Br_4,2NaBr,6H_2O$	95,330	
$Pt,Cl_2,2KCl$	45,170	Salts corresponding with the chloride and bromide.
$Pt,Cl_2,2AmCl$	42,550	
$Pt,Br_2,2KBr$	32,310	

(*b.*) *Heat of Formation of the Double Haloïd Salt.*

Reaction.	Heat evolved.	Explanation.
$PtCl_6K_2$	−13,760 units	
$PtBr_6K_2$	−12,260 „	
$PtCl_6Na_2$	+ 8,540	These numbers give the evolution of heat on addition of 6 mols. of water of crystallisation. $PtCl_6Na_2.6H_2O = 19,170$. $Pt,Br_6Na_2.6H_2O = 18,540$.
$PtBr_6Na_2$	+ 9,990	
$PtCl_6Na_2.6H_2O$	−10,630	
$PtBr_6Na_2.6H_2O$	− 8,550	
$PtCl_4K_2$	−12,220 „	
$PtCl_4Am_2$	− 8,480 „	
$PtBr_4K_2$	−10,630 „	

(*c.*) *Reactions in the Wet Way.*

Reaction.	Heat evolved.	Explanation.
$Pt,Cl_4,2RClAq$	84,620 units	H_2,K_2,Na_2,Am_2, or an atom of the metals of the alkaline earths or of the magnesium series, may be substituted for 2R without any alteration in the evolution of heat.
$Pt,Br_4,2RBrAq$	57,160 „	
$Pt,Cl_2,2RClAq$	41,380 „	
$Pt,Br_2,2RBrAq$	31,840 „	

Reaction.	Heat evolved.	Explanation.
$Pt,O_2,6HClAq$	64,060 units	A molecule of hydrogen may be replaced by two equivalents of the metals named without altering the evolution of heat.
$Pt,O_2,6HBrAq$	80,360 „	
$Pt,O,4HClAq$	31,550	
$Pt,O,4HBrAq$	43,440	
$Pd,Cl_4,2KCl$	79,060	Heat of formation of the double chlorides, the iodide, and hydrated oxides of palladium.
$Pd,Cl_2,2KCl$	52,670	
Pd,I_2,H_2O	18,180	
$Pd,O_2,2H_2O$	30,430	
Pd,O,H_2O	22,710	
$PdCl_4K_2,Aq$	−15,000?	Heat of solution of the double chlorides.
$PdCl_4K_2,Aq$	−13,630	
$Pd,Cl_4,2HClAq$	72,940?	Formation of the chloro-palladium hydrogen acids in aqueous solution.
$Pd,Cl_2,2HClAq$	47,920	
$Pd,O_2,6HClAq$	52,380?	
$Pd,O,4HClAq$	37,640	
$PdO_4H_4,6HClAq$	21,950? „	Evolution of heat on solution of the hydrates in hydrochloric acid.
$PdO_2H_2,4HClAq$	14,930	

Temperature 18°. Pt = 198. Pd = 106.

Theoretical Results.—The haloïd compounds of platinum and palladium form with the hydracids of chlorine, bromine, and iodine, compounds which are soluble in water, and perfectly possess the character of bibasic hydracids, *i.e.*, they form crystalline soluble salts with the alkalis, alkaline earths, and bases of the magnesium series, and more or less insoluble salts with the oxide of lead, mercury, and silver. The isomorphism of several of these groups indicates similarity of constitution, and the heat of neutralisation for the same base is the same as that of hydrochloric acid. The formulæ of the two series of acids are $PtCl_6H_2$ and $PtCl_4H_2$. Tin, mercury, and gold form similar acids, and if the compounds of fluorine were included, silicon and several other elements would be added to the group. The heat of neutralisation of all these acids agrees in that of hydrochloric acid. These bodies are not known in the anhydrous state, but several of them have been obtained as hydrated crystalline acids, *e.g.*, $PtCl_6H_4 + 6H_2O,AuCl_4H + 3H_2O,AuBr_4H + 5H_2O,HgBr_3H + 4H_2O$. They are all decomposed by heat, and yield normally water, haloïd hydracids, and a haloïd compound of the metal; but in many cases the temperature rises so high that the metallic compound is partially decomposed. Some of these acids are decomposed by water, while others possess considerable stability.

It appears to be a general rule that the heat of solution of potassium salts is always more strongly negative than that of the corresponding sodium salts, and that the differences of the heats of solution of the corresponding haloïd salts of potassium and sodium are simple multiples of a constant. Thus—

Units.

$K_2Cl_2,Aq—Na_2Cl_2Aq$ .... = − 8,880 + 2,360 = − 6,520 = − 2·3260
$K_2Br_2,Aq—Na_2Br_2Aq$ .. = −10,160 + 380 = − 9,780 = − 3·3260
$K_2I_2,Aq—Na_2I_2Aq$ ...... = −10,220 − 2,440 = −12,660 = − 4·3165
$PtCl_6K_2,Aq—PtCl_6Na_2,Aq$ = −13,760 − 8,540 = − 22,300 = − 7·3186
$PtBr_6K_2,Aq—PtBr_6Na_2,Aq$ = − 12,260 − 9,990 = − 22,250 = − 7·3179

The explanation of this fact is that the sodium salts are not fully saturated compounds like the potassium salts: they have a tendency to combine with water, and this tendency is least with sodium chloride, greatest with the haloïd compounds of sodium and platinum. The formation of potassium-palladium chloride is accompanied by a greater evolution of heat than that of potassium-platinum chloride, while, on the other hand, it is just the reverse in the case of the dichlorides. This would follow from the fact that palladium forms the chloride, platinum the dichloride most readily. The heat evolved in each case is as follows:—

	Platinum.	Palladium.
Chloride	·45170 units	2·26335 units.
Dichloride	2·44750 „	3·26353 „

Of much greater importance is the result of the comparison of the difference of evolution of heat in the formation of compounds of two different stages of the same metals, in the case, for instance, of the passage of the compounds of gold, mercury, palladium, and platinum from a lower to a higher stage by addition of a molecule of chlorine, bromine, and iodine, the evolution of heat is as follows:—

	Chlorine.	Bromine.	Iodine.
Mercury	6·8858	4·8822	3·8793
Platinum	5·8866	3·8983	
Palladium	3·8797	—	—
Gold	2·8505	1·8930	—

A molecule of chlorine, therefore, gives in these allied reactions an unequal evolution of heat in the proportion of 2 : 3 : 5 : 6, bromine of 1 : 3 : 4, &c. The mean constant is the same in all, 8,850 units.

G. T. A.

Thermo-chemistry of Aniline and other Bodies of the same Group. By W. Louguinine (*Compt. rend.*, lxxxiv, 1159—1161).—The author's determinations show that aniline is a feebler base than ammonia, by which it is almost completely displaced in the cold. On the other hand, aniline displaces the ammonia of ammoniacal salts when heat is applied. This apparent anomaly is explicable by supposing that the acid is so divided between the two bases in the solution, that much aniline and little ammonia exist in the free state. In the cold this condition persists, but when heat is applied, the free ammonia is volatilised and the equilibrium destroyed, so that a fresh quantity of ammonia is displaced to be volatilised in turn, and so on, until the displacement is complete.

Paratoluidine is not in any notable degree displaced by aniline from its combination with hydrochloric acid, but it is completely displaced by soda. R. R.

Researches on the Law of Avogadro. By A. WURTZ (*Compt. rend.*, lxxxiv, 1262).—The author, in a recent paper (p. 404 of this vol.) has shown that chloral hydrate is dissociated as soon as it assumes the state of vapour, and that potassium oxalate does not lose water in this mixed vapour, if its tension of dissociation at a particular temperature is equal to or less than the tension of the water-vapour in the dissociated chloral hydrate at that temperature. The experiments were made at 79° and at 100°, but the latter only were then given. He now gives the results of the experiments made at 79°.

At 79° the tension of dissociation of potassium oxalate is very small, and, if the salt be perfectly dry and free from air, the depression produced does not exceed 3 mm.

Two experiments were made; in the first the depression produced by the introduction of the potassium oxalate into the chloral hydrate vapour was about 8 mm.; in the second it was 4 mm.

The experiments made at 100° were also repeated, and a depression of 4 and 6·5 mm. produced. The same oxalate, when heated in a vacuum, produced a depression of 153 mm. These experiments fully confirm the results deduced from those already published, namely, that chloral hydrate undergoes complete dissociation at the moment when it assumes the state of vapour. C. W. W.

Vapour-density Determinations. By W. KNECHT (*Deut. Chem. Ges. Ber.*, x, 978).—In order to see if the isocyanides (carbamines) are polymeric with the cyanides, the vapour-density of isopropyl-carbamine, $C_3H_7-N\equiv C$, was determined, and found to be 2·42, 2·64, 2·38 in these experiments (calculated for C_3H_7NC, 2·38). Diethylnitrosamine gave the density 3·36, 3·35 (calculated for $N(C_2H_5)_2NO = 3·53$), wherefore it is not expressed by a doubled formula, although the greater decomposibility of nitroso-bodies compared with the corresponding nitro derivatives, might lead one to expect that the former are more complex bodies. The boiling point of alcohol is depressed 62° by conversion into $C_2H_5.O.NO$ (b.p. 78° and 16° respectively); that of diethylamine is raised 120° by nitroso-substitution, forming $(C_2H_5)_2N.NO$. From this the author argues that it might be anticipated that the latter body is a polymeride, which is not borne out by the above numbers. C. R. A. W.

[*Note by Abstractor.*—It has been pointed out by the abstractor (this *Journal*, 1875, p. 228, from *Phil. Mag.* [4], xlviii, 401) that the replacement of the hydrogen of hydroxyl in organic compounds by methyl (*hydroxylic methylation*) is accompanied by an absorption of heat, and consequently by a reduction in boiling point, whilst the similar replacement of non-hydroxylic hydrogen by CH_3 (*hydrocarbonous methylation*) is accompanied by evolution of heat and rise in boiling point. The hydrogen of ammonia would seem from the above instances to be comparable with "hydrocarbonous hydrogen" (hydrogen associated directly with carbon), and not with hydroxylic hydrogen, whilst the group NO is comparable with CH_3, producing lowering of boiling point on substitution for hydroxylic hydrogen ($C_2H_5.OH$ and $C_2H_5.O.NO$), and raising of boiling point on substitution for ammonic hydrogen ($(C_2H_5)_2NH$ and $(C_2H_5)_2N.NO$). The different effects of nitroso-substitution on the boiling point of alcohol and diethylamine afford, therefore, no more *a priori* evidence of polymerisation than do the analogous different effects of methylation on methylic alcohol, according as $CH_3.O.CH_3$ or $CH_3.CH_2.OH$ is formed, indicate that alcohol itself is a polymeride.] C. R. A. W.

Contributions to the History of Vapour-density Determinations. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, x, 962).—The method recently suggested by G. Goldsmith and G. Ciamician (*Berichte*, x, 641) for vapour-density determinations of bodies of high boiling point by weighing the mercury expelled, was published by the author 16 years ago, and has been frequently used by him and his pupils. A modified apparatus, depending on much the same principle, was invented by W. M. Watts in 1867 (*Laboratory*, 1, 225).

C. R. A. W.

Inorganic Chemistry.

Ammonium Compounds. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 561—566).—This is a reply to a criticism by V. Meyer of a previous paper by Ladenburg and Struve. The author, having repeated some of his experiments, maintains the correctness of the results formerly published. J. R.

On some Metallic Selenides and Tellurides. By J. MARGOTTET (*Compt. rend.*, lxxxiv, 1293).—(1.) *Zinc telluride.*—ZnTe. Tellurium and zinc combine, with incandescence, at a temperature between the melting points of the two substances. The resulting mass has a metallic lustre, and gives a cinnabar-red powder. When it is heated in a porcelain tube in a gentle current of hydrogen, ruby-red crystals are deposited in the cooler parts of the tube. These crystals are regular hexagonal prisms with trihedral summits. Sp. gr. 6·34 at 15°.

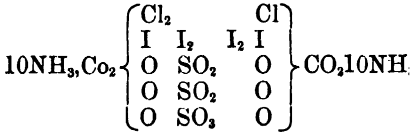
The crystals were dissolved in concentrated nitric acid, the solution evaporated to dryness, the tellurium precipitated by sulphurous acid, and the zinc by sodium carbonate.

(2.) *Cadmium Telluride.*—CdTe.—Prepared by heating cadmium with tellurium to about 500°. The product is amorphous, and has a metallic lustre. Crystals can be obtained in the same way as with the zinc compound. They are black, very brilliant, hexagonal prisms, belonging to the regular system, and exhibiting octohedral and cubical faces. Sp. gr. 6·20 at 15°. The composition was determined as with the previous compound.

(3.) *Zinc Selenide.*—ZnSe.—When selenium and zinc are heated together, they do not easily combine, the selenium floating on the zinc and gradually distilling off, leaving the zinc covered with a layer of yellow selenide. It is more easily prepared by passing hydrogen selenide over zinc heated to redness in a porcelain tube; the combination is accompanied by the disengagement of a large quantity of heat. Thus prepared, it is a yellow amorphous powder, which, when heated in a gentle current of hydrogen, is converted into reddish-yellow crystals of exactly the same form as the corresponding telluride. Their specific gravity at 15° is 5·40.

(4.) *Cadmium selenide*, CdSe, is prepared in the same way as the zinc compound, and forms dark-red, almost black crystals, which arrange themselves regularly, so as to produce striated laminæ in two directions at right angles to one another. Their sp. gr. is 5·80. When they are examined under the microscope between two Nicol's prisms, whose principal sections are crossed, it is seen that extinction of the light takes place when the striæ are parallel or perpendicular to the plane of polarisation; in all other positions the crystals transmit yellow or red light. They do not, therefore, belong to the regular system, unlike the three preceding compounds. C. W. W.

Herapathite and Similar Acid Periodides. By S. M. Jörgensen (*J. pr. Chem.* [2], xv, 418—435). See this *Journal*, 1877, i, 210 and 713.—Gibbs and Genth (*Silliman's Journal* [2], xxiii, 321) have described an "acid sulphate of purpureo-cobalt" obtained by mixing purpureo-cobaltichloride with concentrated sulphuric acid, and after the cessation of evolution of chlorine, adding twice the volume of water. The author finds that three sulphates are formed in this way, one acid and two neutral, and that they all contain $10NH_3,Co_2$, and two atoms of chlorine. When the mixture of these sulphates is dissolved in water, with addition of a little dilute sulphuric acid, and iodine dissolved in hydriodic acid is added, a precipitate resembling herapathite is obtained, which consists of dark olive green plates, with metallic lustre. These crystals polarise light. The formula assigned to them is:—



$$10NH_3,Co_2\left\{\begin{matrix} Cl_2 & & & Cl \\ I & I_2 & I_2 & I \\ O & SO_2 & & O \\ O & SO_2 & & O \\ O & SO_3 & & O \end{matrix}\right\}CO_2 10NH$$

This periodide is insoluble in strong alcohol and ether, and with difficulty in water. It gives a faint brown colour to carbon disulphide. A similar compound may be obtained containing $4NH_3,Pt$.

The acid periodides contain iodine in two forms, *i.e.*, as hydriodic acid, and in the free state, and belong, therefore, to the class of bodies known as "molecular compounds." Many chemical compounds, however, correspond in properties with the periodides, such as potassium-platinum cyanide, which combines directly with two atoms of iodine. Several double salts of ammonium and platinum with iodine also show that no definite line can be drawn between the periodides and chemical compounds. If the periodides are to be looked upon as chemical compounds, the theory of their constitution must depend upon the varying atomicity of iodine.

Several pages of the crystallographic characters of the iodides are appended to the paper. G. T. A.

Silver-ultramarine. By K. HEUMANN (*Deut. Chem. Ges. Ber.*, x, 991—994).—When ultramarine is boiled with a solution of silver nitrate, or better still heated with it for some hours to 120° in closed tubes, it is converted into a mixture of a yellow body and small particles of metallic silver. The latter may be removed either by levigation or by digesting the mixture, first with a solution of iodine in potassium iodide, and then dissolving the silver iodide with potassium iodide. The purified compound consists of microscopic, lemon-yellow, transparent globules, containing—

Ag	47·89 — 48·08
Al	9·00 — 9·21
Na	0·89 — 1·17
S (total)	4·68
S (as sulphate)	0·67
Si	10·46

It is, therefore, an ultramarine in which the sodium is replaced by silver. Dilute acids decompose it, with separation of gelatinous silica and silver sulphide. On using hydrochloric acid, the precipitate contains silver sulphide and chloride, a trace of sulphur dioxide being evolved, but no hydrogen sulphide. Caustic soda blackens the substance, silica, alumina, and a little silver oxide going into solution; while a mixture of the latter and silver sulphide remains behind. When green ultramarine is used, similar results are obtained, but the reaction proceeds much more slowly. C. S.

The Nitrates of Bismuth. By M. YVON (*Compt. rend.*, lxxxiv, 1161—1164).—A sub-nitrate of bismuth of constant composition, prepared by the author as described in the paper, was found by him to correspond with the formula $4B{:}NO_4.H_2O$. He considers this compound to be the normal nitrate of bismuth; the acid or soluble nitrate being regarded as merely a combination of the insoluble salt with nitric acid, which therefore he supposes to enter into the combination under two forms: one portion immediately united with the bismuth, and the other portion joined to the compound thus produced, and forming the acid salt. The latter portion of nitric acid is capable of easy separation, which may be effected either by addition of water, by heat, or by contact of calcium carbonate (or other earthy carbonate), when the more stable sub-nitrate is in each case precipitated.

R. R.

Observations on M. Yvon's Paper on the Nitrates of Bismuth. By A. DITTE (*Compt. rend.*, lxxxiv, 1317).—The author claims to have obtained most of Yvon's results (published in *Compt.*

rend., lxxxiv, 1161), and to have published them in his paper (*ibid.*, lxxxii, 956), in which he proved that the nitrates of bismuth are by no means so numerous as was formerly supposed. The nitrate $2Bi(NO_3)_3.3H_2O$ is decomposed by water into nitric acid and the basic nitrate $Bi(NO_3)_3.Bi_2O_3.\frac{3}{2}H_2O$, which is further decomposed, with formation of $2Bi(NO_3)_3,5Bi_2O_3$, upon which water has no further action. C. W. W.

On the Oxides of Iron. By H. MOISSAN (*Compt. rend.*, lxxxiv, 1296).—Ferric oxide prepared from the oxalate, when heated for half an hour to 350° in a current of hydrogen, furnishes the magnetic oxide; if it be heated for twenty minutes to 500°, ferrous oxide is produced in the pyrophoric state. Thus prepared the latter decomposes water, slowly at ordinary temperatures, more rapidly at 100°. In contact with nitric acid, vivid incandescence takes place. With carbonic acid at 500° it forms carbonic oxide and magnetic oxide of iron: $3FeO + CO_2 = Fe_3O_4 + CO$, a reaction which explains why ferrous oxide cannot be obtained by heating the carbonate, unless the heat be very gentle. Pyrophoric ferrous oxide displaces a part of the ammonia in ammonium sulphate, forming ammonio-ferrous sulphate. Carbonic acid has no effect on it at the ordinary temperature, nor does exposure to a temperature of 450° in an atmosphere of nitrogen deprive it of its pyrophoric properties.

If ferric oxide be reduced by hydrogen at 700°, non-pyrophoric metallic iron is produced. Carbonic oxide produces the same effects as hydrogen, producing magnetic oxide at 350°, pyrophoric ferrous oxide at 500°, and metallic iron at 700° to 800°.

The same results are obtained when the reductions are effected at the same temperature, but for different lengths of time; thus at 440°, ferrous oxide is obtained after six hours, and metallic iron after twelve hours reduction; at 350° magnetic oxide is obtained after one hour, ferrous oxide after ten hours, and metallic iron after thirty-six hours.

The author believes that the pyrophorus of Magnus consists of ferrous oxide: for if pyrophoric iron prepared at 440° be heated to about 700°, it loses its pyrophoric properties. C. W. W.

Separation of Arsenic from Nickel and Cobalt. By F. WÖHLER (*Deut. Chem. Ges. Ber.*, x, 546).—The following method has the advantage of dispensing with the use of hydrogen sulphide:—The arsenical ore is dissolved in aqua regia; any great excess of acid is driven off by evaporation, and the boiling-hot solution is precipitated with sodium carbonate. The precipitate, after washing, is treated, while still moist, with excess of a strong solution of oxalic acid, the effect of which is to convert the nickel and cobalt into oxalates, whilst the whole of the arsenic goes into solution, together with any ferric oxide present. The mixed oxalates are to be thoroughly washed, and may then be separated by means of ammonia.

If copper be present, it may be separated by means of finely divided iron, before the precipitation with sodium carbonate. J. R.

Recovery of Platinum from Chloroplatinates. By E. DUVILLIER (*Compt. rend.*, lxxxiv, 444).—In order to recover the platinum from chloroplatinates, the latter may be reduced by boiling them in alkaline solution with an alkaline formate. The best proportions for reducing the potassium salt are: 100 grams of chloroplatinate, 50 grams of sodium formate, 50 c.c. of soda-solution 30° B., and one litre of water. The platinum salt is added in small portions at a time to the boiling solution. J. W.

Mineralogical Chemistry.

Reproduction of Albite. By P. HAUTEFEUILLE (*Compt. rend.*, lxxxiv, 1301).—When a mixture of tungstic acid and a very alkaline silico-aluminate of soda is heated to dull redness, the tungstic acid combines with part of the alkali, and if the silica and alumina are in the proper proportions, the product has exactly the same composition as natural albite, the excess of tungstic acid not being able to remove any of the remaining soda. The crystals produced are microscopic, but if they are kept for a long time in fused sodium tungstate they increase perceptibly.

Another method of preparation is to heat to dull redness for several days a mixture of six equivalents of silica, one equivalent of alumina, and a small quantity of sodium tungstate, and to remove the excess of tungstic acid by boiling with water and subsequent fusion with acid potassium sulphate. The following are the comparative measurements of natural and artificial albite:—

	Artificial.	Natural. By Des Cloizeaux.
m/t	120° 40′ to 120° 45′	120° 47′
t/g′	119° 40′	119° 33′
p/g′	93°	93° 36′
m/p	69° to 68° 50′	69° 10′

Almost all the crystals are macles, resembling those of the albite of Dauphiné. The density of the crystals is 2·59—2·66, and their action on light is exactly the same as that of natural albite. C. W. W.

Analysis of Emeralds and Beryls. By C. GREVILLE WILLIAMS (*Chem. News*, xxxv, 256—259).—Among the various methods which have been proposed for separating glucina from alumina, the following three have been especially used in the most important researches. These are the carbonate of ammonium process, the hydrate of potassium, and the chloride of ammonium process. The author's paper is devoted to a study of the first of these, namely, the carbonate of ammonium process. The following are the principal problems which he has endeavoured to solve:—(1.) Is glucina permanently soluble in a solution of ammonium carbonate? (2.) Does glucina confer its solubility on alumina, or does alumina confer its insolubility on glucina? (3.) With what amount of accuracy can a mixture of glucina

and alumina be separated by means of ammonium carbonate? (4.) How do solutions of glucina and alumina behave with barium carbonate?

With regard to the first question, namely, the permanent solubility of glucina in ammonium carbonate, the author's experiments lead him to affirm unhesitatingly that one decigram of pure glucina is permanently soluble in 25 c.c. of a saturated solution of ammonium carbonate. Variations in temperature do not influence the solubility of glucina in solution of ammonium carbonate. The question whether glucina confers its solubility on alumina was considered to be best answered by treating with carbonate of ammonium a mixture containing a great excess of glucina. It was found that the glucina, although in such great excess, had not conferred its solubility on the alumina; but, on the contrary, the alumina had conferred its insolubility on the glucina, even when mixed with glucina to the small extent of 3 per cent. Experiments made with reference to the third question, namely, with what amount of accuracy can a mixture of glucina and alumina be separated by means of ammonium carbonate, showed that results to within half a per cent. of the truth can be obtained by means of the carbonate of ammonium process, if a sufficient number of extractions be made. In the author's experiments seven extractions with carbonate of ammonium were made. With regard to the last question, the author undertook three experiments. (1.) Precipitation of alumina in the cold by carbonate of barium; the result proving that alumina is completely precipitated in the cold by carbonate of barium. (2.) Precipitation of glucina in the cold by carbonate of barium; this experiment confirmed the observation of Awdejew, that glucina is but imperfectly precipitated by carbonate of barium in the cold. (3.) Precipitation of a mixture of glucina and alumina in the cold, by carbonate of barium. The result showed that alumina, as in the experiment with carbonate of ammonium, communicates much of its insolubility to the glucina. Assuming only the portion precipitated by carbonate of barium to be accounted for in the analysis of a beryl containing 28·89 per cent. of the mixed earths, only 26·96 would be obtained, the loss being 6·67 per cent., which, as has been shown, would fall chiefly upon the glucina, if the operation were conducted in the cold. This loss is, however, variable, and appears to depend, to some extent, upon the relative proportions of the two earths. D. B.

Notes on Specimens of Chrysocolla. By W. HUTCHINGS (*Chem. News*, xxxvi, 18).—Many pieces of the above ore are found in Lower California, consisting of two very distinct varieties of chrysocolla, one part being hard, vitreous, and of a fine bluish-green colour, while another portion is soft and earthy, of a pale bluish-white colour, and so light and porous that it will float for some time upon water. One specimen was found to absorb 85·5 per cent. of its own weight of water. Dana mentions the occurrence of similar specimens, and gives an analysis by Scheerer, who mentions that this ore occurs with felspar, and is supposed to have resulted from the action of copper sulphate on the felspar. The author has never found any felspar among this ore, although many of the earthy specimens do certainly in some respects much resemble decomposed felspar in appearance.

The following is an analysis of a vitreous and an earthy specimen, the finely powdered minerals being dried at 95° for some hours:—

	SiO_2.	CuO.	PbO	Fe_2O_3.	Al_2O_3.	ZnO.	CaO.	MgO.	H_2O.
Vitreous......	67·07	24·95	0·26	0·27	0·55	0·09	0·81	0·37	5·85 = 100·22
Earthy	46·45	39·15	0·41	0·48	3·65	0·10	0·80	0·82	7·99 = 99·85

The mineral of these deposits is doubtless "true chrysocolla" mixed with large amounts of opal silica, and containing a certain amount of silica very finely disseminated through the mineral as quartz and chalcedony. The proportion of this, roughly estimated, is about 3 per cent. in the vitreous and less than 1 per cent. in the earthy variety. The earthy variety is more or less fusible, apparently owing to the increase in alumina, while the vitreous mineral is not in the least degree fusible. In addition to the minerals which the author has already described as occurring in the chrysocolla-ore from Lower California, a small quantity of what appears to be another variety of the "kupferpecherz" has been found. Its hardness is 2 to 3, with black streak, and is easily fusible before the blowpipe, differing in these respects from the variety formerly described (*Chem. News*, xxxiv, 141). Its composition is as follows:—

SiO_2.	CuO.	Fe_2O_3.	TuO.	CaO.	MnO.	O	CaO.	MgO.	SO_3.	H_2O.
11·95	14·20	9·35	0·80	0·95	38·53	7·89	2·41	2·35	0·16	11·61 = 100·20

It is found only in thin layers, alternating with chrysocolla and fibrous gypsum.

D. B.

On two New Niobates. By J. L. SMITH (*Compt. rend.*, lxxxiv, 1036).—The author, in his researches on the niobates of the United States, has discovered two new species, found in North Carolina, which he has named Hatchettolite and Rogersite. Hatchettolite occurs in regular octohedrons, associated with euxenite and samarskite, but no cleavage has been discovered in the eight or ten crystals hitherto examined. H = 5; sp. gr. = 4·851. The author gives three analyses, from which it will be perceived that the chief difference between hatchettolite and pyrochlore is the predominance of uranium oxide in the first of these minerals.

NbO_5.	NO_3 and SnO_2.	WO_3.	CaO.	YO.	FeO.	K_2O.	Loss on ignition.	Lead.
66·01	0·75	15·20	7·72	2·00	2·08	0·50	5·16	trace = 99·42
67·86	0·60	15·63	7·09	0·86	2·51	1·21	4·42	trace = 100·18
67·25	0·91	16·01	7·11	0·64	2·12	—	5·02	trace = 99·06

Rogersite is found as a white incrustation on samarskite and euxenite, only small quantities having been obtained up to the present time. H = 3·5. Sp. gr. = 3·313. Two approximate analyses made on small quantities of the mineral give—

	I.	II.
Niobic acid	18·10	20·21
Yttria, &c.........	60·12	—
Water...........	17·41	16·34

Rogersite is very interesting, as being the first niobate in which so large a proportion of water has been found; it is evidently a product of the decomposition of samarskite or euxenite, or of both.

J. M. T.

Diffusion of Strontium in Nature, at the Present Time and at the various Geological Epochs. Consequences relative to Mineral Waters. By L. Dieulafait (*Compt. rend.*, lxxxiv, 1303).—1. Strontium exists in mineral waters and in the sea in the forms of carbonate and sulphate. As carbonate it can be recognised in 100 c.c. of sea-water, and as sulphate in 4 c.c.

2. The gypsums which are formed in salt marshes contain so much strontium that 1 mg. gives the spectrum of strontium with perfect clearness.

3. In the formation of rock-salt by the spontaneous evaporation of seas, the strontium accumulates in the first deposit ($CaCO_3$), and particularly in the second ($CaSO_4$). None is present in the later formations—sea-salt, potassium chloride, magnesium chloride, &c., or in the last mother-liquors.

4. The carbonate and sulphate of calcium which exist in the sea always contain strontium; and, as the hard parts of marine animals are necessarily derived from this source, they also contain strontium, in quantity sufficient to be seen in 1 centigram of substance.

5. The fossil remains in marine formations from the palæozoic strata up to the present time also contain strontium.

6. Numerous specimens of gypsum from different strata all gave the spectrum of strontium with quantities of substance less than 1 centigram. Specimens of gypsum from different parts of the same formation always contain the same quantity of strontium, showing that it is equally diffused throughout the entire mass.

7. Seventy-one specimens of mineral waters were all found to contain strontium, in quantity sufficient to be recognised in less than 100 c.c. of water.

C. W. W.

The Distribution of Zircon in Rocks. By A. E. Törnebohm (*Jahrb. f. Min.*, 1877, 97).—In granites are often observed microscopical grains of a colourless, or brown, strongly refracting mineral, which exhibit brilliant colours in polarised light, and crystallise in the quadratic system. These crystals are considered by the author to be zircon. They exhibit the combinations $P . \infty P . \infty P \infty . 3P$; and some of the larger crystals appear to have a zonal structure. Swedish granite may be said to contain zircon as a constant accessory, whilst zircon also occurs in the granites of Switzerland, Saxony, Tyrol, and North America. Zircon is also found in the gneiss of Sweden, and in the felsite-porphyry, eurite, and hälleflinta of different localities. C. A. B.

The Nordenskiöld Iron-mass, and the Occurrence of Native Iron in Basalt. By K. J. V. Steenstrup (*Jahrb. f. Min.*, 1877, 91—94).—According to Nordenskiöld, the masses of iron found near Blaafjeld, on the south coast of the island of Disco, are meteoric, and enclosed in a basaltic vein, which must have been in a pasty condition at the time of the meteoric fall. From the analyses of the rocky mass surrounding the iron, Nordenskiöld came to the conclusion that the latter was enclosed by a silicate resembling eucrite. Steenstrup concludes, from his investigation into the geognostic character of the district into which the meteoric iron-masses were found, that they were not contained in a vein of basalt, but were only covered by that rock. The iron was found occurring in round lumps, also in plates having a horizontal and vertical position, and in dendritic forms on the surfaces of clefts in the rock. No rounded masses of basalt or eucrite were found in the basalt, and the so-called eucrite was not found to be separated from the basalt by a sharply-defined rust-like rind, but rather was intimately combined with it, the passage from one to the other being very gradual. The author contends that these iron-masses are accessories of the basaltic rock in which they occur, and are not of meteoric origin, as he found, on examination of the basalt of the north coast of Disco (in the neighbourhood of Assuk, on the Waigattfjord) that particles of iron (not exceeding $\frac{1}{2}$ mm. in length, and $\frac{1}{4}$ mm. in breadth) occurred in it. These particles, mostly consisting of metallic iron, contained sulphur, distinct traces of copper, and cobalt, and faint traces of nickel, with much phosphoric acid. Iron particles were not found in any other basaltic rocks on the island except those of Blaafjeld and Assuk. The author states also that the iron of the basaltic rocks is telluric, and therefore that the iron-masses of Nordenskiöld are the same, as they have doubtless "weathered" out of their basaltic matrix, whilst their size and the higher percentage of nickel entering into their composition is accidental. Widmanstätt's figures can also occur on telluric iron-masses. Meteoric iron-masses could not have retained their form after the solidification of the pasty basalt into which they had fallen, and especially when they had "weathered" out and been acted upon by the sea and ice. Referring to the analyses of these iron-masses by Nauckhoff, the author considers the alleged occurrence of troïlite to be doubtful, as the material analysed was impure, and the amount of sulphur was estimated by loss, whilst the occurrence of spinelle is certainly no proof of meteoric origin. The basalt is undoubtedly changed in its character in the immediate neighbourhood of the iron, and in addition to the ordinary minerals already mentioned, it also encloses graphite; but the author did not find any indication of the presence of anorthite, as stated by Nauckhoff: hence he considers the conclusion arrived at by Nordenskiöld, that "the basalt enclosed round masses of eucrite" to be doubtful. Steenstrup contends that the iron-masses in question must have been formed simultaneously with the basalt surrounding them, or that they resulted from the separation of iron from the basalt by chemical action, and the grains of metal so formed may have become eventually the huge masses which they now are by concretionary forces. This opinion is in a measure supported by the discovery of a mass of nickeliferous magnetic iron-pyrites, 28,000 kilos. in weight, in an olivine-basalt near Igdlokunguak, on the Waigatt; and it is a well known fact that iron can be obtained in the metallic state from its combinations by the reducing action of organic matter. The basalt of Blaafjeld and Assuk contained a considerable amount of graphite, which might have been derived from organic matter, and some of the clefts observed in it have been undoubtedly filled with iron after the solidification took place.

C. A. B.

The Basalt of the Schiffenberg, near Giessen. By A. WINTER and W. WILL (*Jahrb. f. Min.*, 1877, 102—103).—From a macroscopical examination it was observed that the violet-black, fine-grained basalt of this district consisted of a ground-mass, in which augite, grains and fragments of olivine, laminæ of magnetite, and plates of titanite were disseminated. The drusy hollows in this rock contain small crystals of phillipsite, gismondine, mesotype, arragonite, and calcite. From the microscopical examination of this rock it was observed that the ground-mass consisted of triclinic felspar, augite, and magnetite, and imbedded in it were olivine crystals, which were partially decomposed into serpentine, reddish-brown augite crystals, colourless triclinic felspar crystals, many grains of magnetite and titanite, and here and there isolated needles of apatite. Sp. gr. 2·902. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.
44·04	15·31	3·38	9·09	10·33	11·05	1·69	1·97	2·94	0·18=99·98

The authors state further that they specially sought for and found 4·75 per cent. of titanic acid, 0·44 per cent. of sulphides of the lead and arsenic groups, 0·50 per cent. of phosphoric acid, equal to 1·09 per cent. apatite.

C. A. B.

Microscopical Examination of the Uralite-Porphyry of Vaksala. By E. SVEDMARK (*Jahrb. f. Min.*, 1877, 99—100).—A macroscopical examination of the uralite-porphyry of Vaksala proved it to consist principally of a dark-green diorite-like ground-mass, with interposed plagioclase, hornblende, and uralite. Under the microscope it appeared as a fine crystalline mixture of green or brown acicular and foliated hornblende, with plagioclase, quartz, magnetite, titanite, iron-pyrites, epidote, and apatite interspersed here and there. Most of the constituents exhibit a more or less developed decomposition, and some of them may doubtless have arisen through the decomposition of others. The author comes to the following conclusions from his investigations:—

1. Uralite is a pseudomorphous formation of hornblende after augite, the form of the latter mineral being retained.

2. The hornblende is often changed to a secondary product, resembling chlorite or viridite.

3. The change always commences on the exterior, and generally follows the clefts in the augite, or its enclosures.

4. The magnetite is the result of the various changes which have taken place.

The uralite of Vaksala never occurs microlitic, and is of two colours, viz., green and brown, sometimes both colours on one specimen. Sections made parallel to the vertical axis rarely exhibit any fibrous striation, but appear to be built up of broad or narrow columnar prisms, whence the uralite of this district differs from that of other localities. Irregular augite kernels occasionally occur enclosed in a uralite section, and the opaque, whitish substance which often accompanies titanite (named leucoxene by Gümbel) is also present. The author remarks that this leucoxene is also found transparent, yellowish, faintly lustrous, and apparently isotropic. Numerous fluid enclosures (some movable) are also observed. C. A. B.

The Crystalline Rocks of Minnesota. By A. STRENG and J. H. KLOOS (*Jahrb. f. Min.* 1877, 31—56).—The rocks described in this paper are situated partly in the Upper Mississippi district and on its tributary the Sauk-River, partly on the westerly bay of Lake Superior, the mouth of the St. Louis river, and lastly on the St. Croix river between Minnesota and Wisconsin. They represent the Laurentian and probably the Huronic formations, and include every variety of granite, syenite, diorite, and gabbro, whilst diabase is remarkable for its absence. The syenite-granites of St. Cloud and the Sauk Rapids form long, rounded, gently-rising mounds (the spaces between the mounds being filled with diluvial deposits, or low rocky reefs). At the village of Sauk Rapids three narrow parallel veins of black melaphyr penetrate the syenite-granite. At Watab (a half deserted village six miles distant from the last-mentioned locality) higher and broader mounds are observed, the rocks being more rugged and wild and densely wooded, consisting of augite-quartz-diorite, syenite-granite and melaphyr.

The authors observe that the white granite of Watab described in the geological survey of Minnesota differs entirely from the granite obtained by them from this locality, as it occurs but very sparingly, and does not include the same minerals in its constitution.

It also appears that veins of the granitic rocks of this district penetrate hornblendic rocks of a fine-grained texture. At the village named Little Falls, a complex of schistose rocks is observed, the nature of which alters somewhat both in the "dip" and the "strike." Roofing-slates are widely spread; north of Little Falls mica-slate predominates, whilst south of that place the layers partake of the character of a fine-grained gneiss, alternating with a fine augite-diorite. The crystalline roofing-slates near Little Falls are lenticular, and enclosed in quartz-diorite. They in their turn enclose small garnets, which appear to be most numerous on the outer surfaces of the lenses, and if the latter are large, there is generally a hollow space in the centre of each filled with crystals of quartz. Three and a-half miles west of

St. Cloud on the Sank-River, there is a syenite-granite rock having a reddish colour and porphyritic structure, and accompanying it there are various granitic rocks. The finest specimens are found at Coldspring (a small village 15 miles west of St. Cloud), the river here cutting a parallel series of mounds having almost an easterly strike. The rocks at Coldspring are a fine-grained porphyritic granite, and a very coarse-grained syenite-granite, the latter continuing as far as Richmond, where it covers a dark, fine-grained augite-diorite. The syenite-granite of Richmond is much weathered and occasionally covered with a plastic clay belonging to the chalk formation. The River St. Louis has its source in the north-east of Minnesota, south of Vermilion Lake, in a region of granite, gneiss, and crystalline slates, whence it flows through a most lovely and romantic series of " dales " towards Lake Superior, into which it falls. The deposits or layers consist of a series of " roofing-slates " and a grey, fine-grained rock somewhat resembling quartzite in appearance, but whose composition has still to be determined. On arriving at the foot of the plateau, which is situated at the mouth of the St. Louis river, a high wall of rocks is observed, which goes by the name of " Duluth-Granite " (much used for ornamental purposes), described by the authors under the name of " hornblende-gabbro."

The lowermost rock, which is washed by the water of the lake, was described in 1871 as porphyritic; but a more complete examination proves it to be melaphyr-porphyry, which here and there passes into a beautiful amygdaloïdal formation, without any distinct line of demarcation. Besides the hornblende-gabbro and the melaphyr-porphyry, there is a third rock of a blackish colour lying upon the melaphyr-porphyry, exhibiting at the same time a very distinct line of demarcation between them. This rock is melaphyr. On the westerly bay of Lake Superior the rocks belong to the final Huronic series, and the primary silurian. One hundred miles from this locality, and on the St. Croix river (between Minnesota and Wisconsin), occurs a similar melaphyr-porphyry forming the lower layer of the sandstones and conglomerates of the lower silurian. Like the melaphyr-porphyry of Duluth, at the mouth of the St. Louis river, the last-mentioned rock often occurs amygdaloïdal, enclosing quartz in its cavities, whilst the amygdaloïd of Duluth enclosed calcite, epidote, and a mineral substance rich in iron and manganese.

The authors then give a lengthy and minute macroscopical and microscopical description of all the above-mentioned rocks.

C. A. B.

Organic Chemistry.

Miscellaneous Notes. By E. Erlenmeyer (*Deut. Chem. Ges. Ber.*, x, 634—637).—*Water as Oxidising and Reducing Agent.*—When lactic acid is heated with dilute sulphuric acid, it is resolved into aldehyde and formic acid. In this reaction the hydrogen exerts a reducing action on the carboxyl and the hydroxyl, an oxidising action on the rest. As glycollic acid is decomposed in an analogous way, it appears possible that the lowest homologue, carbonic acid, might in a similar way yield formic acid and hydrogen dioxide, which would then be resolved into water and oxygen. This reaction explains very simply the exhalation of oxygen by plants.

Oxidation of Oxyacids.—Markownikoff, as well as Ley and Popoff, have found that the α-oxyacids yield on oxidation carbon dioxide and a fatty acid containing one molecule of carbon less than the original acid. The former believes that in this reaction ketone-acids are formed in the first instance, while the latter believe that a direct oxidation takes place. The author has found that, on oxidising α-oxycaproic, α-oxycaprylic, and diethyl-glycollic acids, they yield first, by taking up the elements of water, formic acid, and aldehydes (or ketones), which are then further oxidised. The β-oxyacids behave partly in the same way, and are partly first resolved into water and an acrylic acid.

Haloïd-substitution Products of the Fatty Acids.—Schorlemmer has shown that the paraffins yield two isomeric substitution-products, from which it appeared probable that fatty acids would also give isomeric products. When butyric and caproic acids are heated with bromine to 140°, they seem to yield such isomerides, while at 100°, at which the action is but slow, the products consist almost entirely of an α-bromo-acid.

Oxidation of Fatty Acids.—Normal caproic acid yields acetic and succinic acids; normal heptylic acid yields the latter, together with propionic acid, which is partly further oxidised to carbon dioxide, formic acid, and acetic acids. C. S.

Reducing Action of Bone Charcoal at Low Temperatures.

By W. Heintz (*Liebig's Annalen*, clxxxvii, 227).—When platinic chloride solution is boiled for some time with freshly ignited animal charcoal, a colourless acid solution results, containing no platinum, and leaving scarcely any residue on evaporation (the charcoal having been previously freed from all matters soluble in hydrochloric acid). A solution of dehydrotriacetone-ammonium platinochloride was partially reduced on boiling with animal charcoal, the platinum becoming platinous chloride, so that the original salt was regenerated on adding chlorine-water. The charcoal, after filtration and washing, left a considerable residue of platinum on incineration. Special experiments showed that neither CO nor CO_2 nor any carbonaceous gas, are produced during the reducing action of charcoal on ferric chloride, which is readily reduced to the ferrous state: for the evolved vapours gave no turbidity in a mixture of calcium chloride and ammonia either before or after passing over red hot copper oxide. [Qy. a sufficient test? the carbonate is not precipitated till after boiling, when only small quantities of CO_2 are present; baryta-water is a much better reagent.—C.R.A.W.] Traces of an organic substance are taken into solution during the reduction of the ferric chloride; the reducing action appears to be mainly due to the hydrogen still left in the charcoal, even after strong ignition. C. R. A. W.

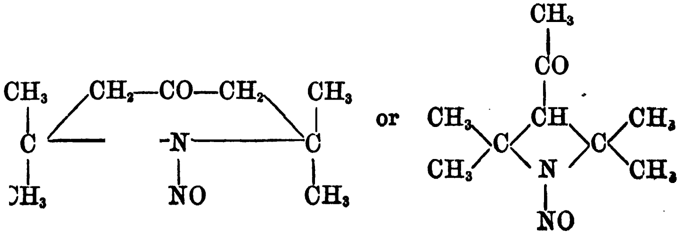
[*Note by Abstractor.*—Recent experiments by the abstractor show that charcoal and chemically prepared carbon (from CO by the action of ferric oxide at a low red heat) retain, even after ignition, occluded gases, especially CO and CO_2, in small quantity: the reducing action of such charcoal may be due to occluded CO, just as palladium charged with occluded hydrogen is a powerful reducing agent.—C.R.A.W.]

Action of Sulphuric Acid on Acetylene. By H. LAGERMARCK and A. ELTEKOFF (*Deut. Chem. Ges. Ber.*, x, 637—641).—By dissolving acetylene in sulphuric acid and distilling the product with water, Berthelot obtained a liquid which he regards as vinyl alcohol, $C_2H_3.OH$. On repeating these experiments, the authors obtained only crotonaldehyde, which was easily oxidised to common crotonic acid melting at 71°. C. S.

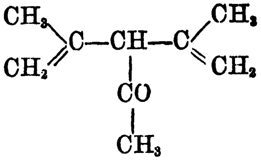
Derivatives of Dextrose and Levulose. By A. P. N. FRANCHIMONT (*Deut. Chem. Ges. Ber.*, x, 994).—Scheffer has obtained in Franchimont's laboratory the potassium and sodium-compounds of dextrose and levulose, which Honig and Rosenfeld have described, and is at present engaged in examining the action of haloïd-ethers and acid chlorides on them. C. S.

Decomposition of Nitrosotriacetonamine by Acids. By W. HEINTZ (*Liebig's Annalen*, clxxxvii, 233).—When neutral solutions of hydrochloride of triacetonamine and potassium nitrite are mixed and left at rest, crystals of nitrosotriacetonamine separate. The author formerly found that on decomposing these crystals with hydrochloric acid, no triacetonamine was reproduced; he now finds that this is erroneous, the parent base being found amongst the products of the reaction to a considerable extent; with sulphuric acid the same result is noticed, but to a smaller extent. The action of hydrochloric acid also gives rise to a difficultly soluble salt, the hydrochloride of a new base, $C_9H_{18}N_2O.HCl.H_2O$, and to some other products not yet fully investigated. C. R. A. W.

Production of Phorone from Nitroso-triacetonamine. By W. HEINTZ (*Liebig's Annalen*, clxxxvii, 250).—When potash acts on nitroso-triacetonamine, the latter splits up into nitrogen, water, and phorone: this substance melted a little under 28°. Nitroso-triacetonamine is apparently represented by one of the two following formulæ:—

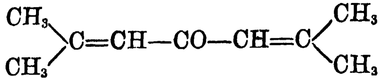


and phorone therefore either by



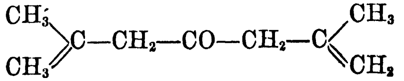
$$\begin{matrix} CH_3 \\ CH_2 \end{matrix}\!>\!C{-}\underset{\substack{|\\CO\\|\\CH_3}}{CH}{-}C\!<\!\begin{matrix} CH_3 \\ CH_2 \end{matrix}$$

or by



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!C{=}CH{-}CO{-}CH{=}C\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

or by



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!C{-}CH_2{-}CO{-}CH_2{-}C\!<\!\begin{matrix} CH_3 \\ CH_2 \end{matrix}$$

C. R. A. W.

Contributions to the History of Chloral. By A. PINNER and F. FUCHS (*Deut. Chem. Ges. Ber.*, x, 1058—1069).—Chloralhydrocyanide is easily obtained by allowing a mixture of chloral hydrate with excess of aqueous hydrocyanic acid to stand for a time, and evaporating the solution. It can be distilled with partial decomposition boiling at 215—220°. Boiled with acetic anhydride for an hour, it yields *chloralacetylcyanide*, $CCl_3.CH(OC_2H_3O).CN$, which may be separated by fractional distillation; the oil which passes over above 160° solidifies to a crystalline mass when repeatedly washed with water. It forms large, colourless rhombohedrons which melt at 31°; it distils without decomposition at 208°; its vapour attacks the eyes strongly even at the ordinary temperature. It is almost insoluble in water, easily soluble in alcohol, ether, acetone, and benzene, less so in petroleum. It is but slowly attacked by alkaline hydrates in the cold, but more quickly when warmed, being resolved into acetic acid and chloralhydrocyanide, the latter subsequently undergoing decomposition in the usual manner.*

When a solution of chloralacetylcyanide in acetic acid is added to concentrated sulphuric acid, and the viscous product after a few days poured into water, a solution is obtained from which ether extracts *acetyltrichlorolactamide*, $CCl_3.CH(OC_2H_3O).CONH_2$. It crystallises in slender needles which melt at 94—95°. It is easily soluble in alcohol, ether, or hot water, less so in benzene, and insoluble in petroleum. *Trichlorolactamide*. $CCl_3.CH(OH).CONH_2$, may be obtained in a similar manner from chloralhydrocyanide. It crystallises in needles which melt at 95—96°. *Acetyltrichlorolactic acid*, $CCl_3.CH(OC_2H_3O).COOH$, is easily prepared by boiling trichlorolactic acid with acetic anhydride. It forms large, colourless crystals which are easily soluble in benzene, but insoluble in petroleum.

As chloralacetylcyanide is not easily attacked by alkalis, it offered a good point of departure for the preparation of chloral derivatives in which the chlorine-atoms are displaced by other groups. The action of aniline on the compound was first studied; on adding

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[*] Some preliminary experiments on the physiological action of chloralhydrocyanide show that it differs from that of chloralcyanhydrate. It would appear, from the results, that it is slowly decomposed in the animal organism, producing tetanus and paralysis of the respiratory organs.

about 2 mols. of aniline to 1 of the chloralacetylcyanide dissolved in alcohol or ether, a powerful reaction takes place accompanied by the evolution of hydrocyanic acid and the formation of a crystalline compound. After removal of the excess of aniline by treatment with dilute hydrochloric acid and crystallisation from alcohol, it was found to have the composition $C_8H_7Cl_2NO$, or that of *dichloracetanilide*, $CHCl_2.CO.NC_6H_6$, and to be identical with the compound which Cech obtained by (*ibid*, ix, 337) the action of aniline on his so-called chloralcyanidcyanate, and regarded by him as an aniline derivative of chloral, $CCl_2(C_6H_6N).COH$. It crystallises in needles, or, by slow evaporation of its alcoholic solution, in large, transparent, lustrous crystals which melt at 117—118°, and may be sublimed by cautious heating. It is insoluble in petroleum and in cold water, but easily soluble in alcohol, ether, and benzene. It is easily soluble in alkaline solutions, and is reprecipitated unchanged on the addition of an acid; boiled with an alkaline solution it evolves the characteristic odour of isocyanobenzene.

Aniline acetate also acts on chloralacetylcyanide, and the product contains two compounds which may be separated by fractional crystallisation from alcohol; of these, one melts at 118° and is identical with the dichloracetanilide above mentioned, whilst the other has the compostion of *monochloracetanilide*, $CH_2Cl.CO.NC_6H_6$. It crystallises in slender needles insoluble in petroleum, slightly soluble in cold water, but very readily in alcohol, ether, and benzene. Although it melts at 84°, the authors regard it as identical with the monochloracetanilide (m. p. 97°) which Tommasi obtained by the action of aniline on chloracetyl chloride. Excess of aniline converts chloralacetylcyanide into a resinous compound, whilst with chloralcyanhydrate small quantities of dichloracetanilide are produced.

Aniline acts in the cold on chloralhydrocyanide, with evolution of hydrocyanic acid, and the mixture, after being heated on the water-bath for a few minutes and poured into cold water, solidifies to a crystalline mass containing a small quantity of dichloracetanilide; the bulk of the product, however, is *trichlorethidenediphenyldiamine*, $CCl_3.CH(NHC_6H_6)_2$, which may be obtained pure by crystallisation from ether alcohol. It possesses the properties ascribed to it by Wallach (*Deut. Chem. Ges. Ber.*, v, 251).

Ammonia in excess passed into a solution of chloralhydrocyanide or chloralacetylcyanide in alcohol, ether, or benzene yields hydrocyanic acid ammonium chloride and *dichloracetanilide*, $C_2H_3Cl_2NO$. An aqueons solution of ammonia produces the same effect. The addition of ammonium acetate to an alcoholic solution of chloralacetylcyanide causes ammonium chloride to be deposited, with evolution of hydrocyanic acid, whilst *dichloracetic ether* is found in the solution together with a small quantity of dichloracetamide. When the acetylcyanide acts on the acetate without alcohol being present, dichloracetic acid appears to be formed, but the investigation of this reaction is not yet completed.

It is known that the aromatic amines act on chloral in the same manner as on aldehydes, water being eliminated and a compound formed in which the oxygen-atom is replaced by two amine-residues:

$$CCl_3.CHO + C_6H_5NH_2 = CCl_3.CH(NHC_6H_5)_2 + H_2O.$$

whilst no satisfactory results have yet been obtained with salts of the aromatic amines. With ammonium salts, however, the case is different. When chloral hydrate and ammonium acetate are heated to boiling, no ammonium chloride is separated, but on pouring the product into water, a crystalline precipitate is obtained having the composition $C_2H_2Cl_3N$. It is only slightly soluble in water, moderately in alcohol and benzene, and very soluble in ether, chloroform, and petroleum. Boiled with alkaline solutions, in which it is insoluble, it gives an odour of amine bases. When gradually heated, it softens at about 80°, and sinters together, but without melting, even at 150°. This compound has in all probability the formula $CCl_3.CHNH$, that of trichlorethidenimide, and is therefore of considerable interest.

When a mixture of urea and chloralhydrocyanide is heated at 105°, it evolves hydrocyanic acid, and a crystalline deposit is formed which is insoluble in most menstrua. It forms white needles, and seems to be *dichloracetylguanidine*, $C(NH)\!<\!\begin{smallmatrix}NHCO.CHCl_2\\NH_2\end{smallmatrix}$. This reaction, however, is not yet completely investigated. C. E. G.

Action of Amines on Chloral. By C. O. Cech (*Deut. Chem. Ges. Ber.*, x, 878—880). A mixture of crystallised toluidine and chloral-cyanide-cyanate soon gets hot, evolves prussic acid, and then solidifies to a mass of glistening scales of *chloral-toluide*, $C_7H_7.NH(C_2Cl_2HO)$. The same body is formed by adding toluidine hydrochloride and potassium cyanide to a solution of chloral hydrate. It is freely soluble in alcohol and ether, crystallising from the latter in silky scales. By adding water to its alcoholic solution, or cooling a boiling aqueous solution, it separates in flakes. It melts at 153°, sublimes in long needles, and is decomposed by boiling alkalis, the isonitril being formed.

Chloralcyanide-cyanate acts violently on ethylamine:

$$C_4H_3Cl_2.N_2O_3 + C_2H_5NH_2 + H_2O = N\begin{cases}C_2H_5\\H\\C_2Cl_2HO\end{cases} + HCN + CO_2 + NH_4Cl.$$

The same body is formed by adding a solution of potassium cyanide to a mixture of ethylamine and chloral. It separates from ether in granular yellow crystals, melting at 45°; it can be sublimed, and is decomposed by boiling with water, acids, and alkalis. C. S.

Hexylchloral. By A. Pinner (*Deut. Chem. Ges. Ber.*, x, 1052—1058).—This compound was obtained by submitting the higher-boiling portion of crude butyl chloral to fractional distillation. Hexylchloral, $C_6H_9Cl_3O$, boils at 212—214°, but has not yet been obtained quite free from butylchloral. It is insoluble in water, but mixes in all proportions with alcohol, ether, and benzene. It does not form a solid hydrate with water, nor a hydrocyanide with hydrocyanic acid, but is decomposed by alkaline hydrates, yielding a formate, a chloride, and a compound of the composition $C_5H_8Cl_2$. Fuming nitric acid oxidises it to a *trichlorocaproic acid*, $C_6H_9Cl_3O_2$; for this purpose the chloral is mixed with twice its volume of nitric acid and allowed to stand for 24 hours, when it is poured into about eight times its volume of water. The oil which separates solidifies after a time, and is then crystallised from a mixture of benzene and petroleum. The acid melts at 64°, and is almost insoluble in water, but very soluble in alcohol, ether, and benzene, less so in petroleum.

This chlorocaproic acid is strongly acted upon by zinc-dust in presence of water, and if hydrochloric acid be then gradually added, the surface of the zinc in the course of a few days becomes covered with long, flat needles of a *hexylenic acid*, $C_6H_{10}O_2$. The new acid melts at 39°, is almost insoluble in water, but very readily soluble in alcohol, ether, benzene, and petroleum. It is formed from the trichlorocaproic acid by the removal of two atoms of chlorine, and the subsequent displacement of the remaining atom of chlorine by hydrogen. Three acids are known which have the same composition as this one, namely, the hydrosorbic acid of Barringer and Fittig, the pyroterebic acid of Rabourdin, and the ethylcrotonic acid of Frankland and Duppa. As far, however, as the small quantity of substance at the author's disposal would permit him to investigate its properties, it would appear to be quite distinct from either of these acids.

There are two ways in which it is possible that hexylchloral might be formed by the action of chlorine on aldehyde: three molecules of aldehyde might condense to form a compound, C_6H_8O, which, by the addition of HCl and Cl_2, would form $C_6H_9Cl_3O$; or monochlorocrotonic aldehyde might be formed, which, together with an aldehyde molecule, might be condensed to C_6H_7ClO, and then take up 2HCl to form $C_6H_9Cl_3O$. The product of the action of chlorine on paraldehyde in the cold was examined most carefully, but no evidence of the formation of monochlorocrotonic aldehyde could be found.

Occasionally considerable quantities of an oil of pleasant odour, boiling at 150°, are present in crude butyric chloral. It has the composition $C_3H_4Cl_2$ and is *allylene tetrachloride.* Allylene dichloride is formed by the long-continued action of concentrated hydrochloric acid on butyric chloral at a high temperature—

$$C_4H_5Cl_3O + H_2O = C_3H_4Cl_2 + HCl + CH_2O_2,$$

and this unites readily with two atoms of chlorine to form the tetrachloride. It is important therefore in the manufacture of butyric chloral to chlorinate the aldehyde at the ordinary temperature, as far as possible, and heat but a very short time. C. E. G.

Contributions to the History of Glyoxylic Acid. By C. Böttinger (*Deut. Chem. Ges. Ber.*, x, 1084—1087).—1. *Action of Hydrocyanic and Hydrochloric Acid on Glyoxylic Acid.*—When hydrochloric acid is added to a mixture of syrupy glyoxalic acid with hydrocyanic acid, carbonic anhydride is evolved in quantity proportional to the hydrochloric acid employed. If sufficient acid is added, and the mixture put aside for some weeks, crystals of ammonium chloride make their appearance, and the solution then yields a small quantity of oxalic acid when agitated with ether; on evaporating it to dryness at 100°, and extracting the residue with absolute alcohol and ether, a solution was obtained, which, on examination, was found to contain glycollic acid. Analyses were made of the calcium and silver salts. The reaction which takes place is, therefore, parallel to that with pyroracemic acid, under similar circumstances (*ibid.*, ix, 1631).

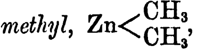
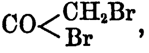
2. When glyoxylic acid is heated with acetic anhydride and sodium acetate, as in Perkin's method for the synthesis of organic acids, a powerful reaction takes place, but neither fumaric nor maleic acid could be discovered in the dark-coloured product, the only substances present, besides oxalic and glycollic acids, being a dark-coloured syrupy compound having an odour of burnt sugar.

3. *Action of Hydrogen Sulphide on Glyoxylic Acid.*—The reaction which takes place has not yet been fully investigated, but the author finds that besides oxalic acid, a syrupy acid containing sulphur is formed by the action of hydrogen sulphide on a dilute aqueous solution of glyoxylic acid agitated with silver oxide. The acid, which is probably "mercaptanglycollic acid," is only partially precipitated by lead acetate. It is easily etherified. C. E. G.

The Preparation of Crystalline Magnesium Acetate and its Fermentation. By L. PATROUILLARD (*Compt. rend.*, lxxxiv, 553—554).—I. Glacial acetic acid must be diluted with at least one-fourth of its volume of water before it dissolves magnesium carbonate. The solution, when evaporated over sulphuric acid, deposits fine crystals of magnesium acetate.

II. A mixture of alcohol and ether precipitates the acetate as an oily layer, which soon solidifies. The crystals deliquesce in moist air, and effloresce in dry air, showing that they contain water of crystallisation.

III. When exposed to air, a solution of magnesium acetate becomes covered with a pellicle, below which solid granular bodies like stalactites make their appearance. The chief product of this fermentation is magnesium carbonate, but magnesium formate is also produced, and the liquid has the smell of methyl alcohol. W. R.

Action of Zinc-methyl on Bromacetyl-bromide. By A. BUTLEROW (*Deut. Chem. Ges. Ber.*, x, 407—409).—In the action of *zinc-methyl*,  $Zn<^{CH_3}_{CH_3}$, on *bromacetyl-bromide*,  $CO<^{CH_2Br}_{Br}$, explosions are very liable to arise, and thus, up to this time, every effort to obtain satisfactory results has been unavailing. Winogradoff has, however, found that these explosions and excessively violent action can be avoided, if at first the reaction be conducted in absence of methyl iodide (generally used to dilute the zinc-methyl and to moderate the action), and the flask be cooled only when the reaction becomes too energetic. Before this, the zinc-methyl was diluted with methyl-iodide, with the intention of moderating the action, and the flask containing the materials was, from the first, strongly cooled.

On adding the bromacetyl-bromide, at first, under these circumstances, no action occurred, merely a solution of the bromide in the zinc-methyl taking place. When considerable quantities of the liquids had become thoroughly mixed in the flask, a violent action commenced, followed generally by an explosion.

By taking the precautions mentioned, all danger is avoided. When the necessary quantities of the liquids are brought together (1 part of $CH_2BrCOBr$ to 3 of $Zn(CH_3)_2$, the flask, with its contents, is allowed to stand for 1—5 weeks, when the resulting fluid is decomposed by water. After one or two days, needle-shaped crystals separate out. On decomposing with water, no oil separates from these crystals, and they probably consist of $Zn{<}^{Br}_{CH_3}$, as analysis indicates. Besides a brominated substance with suffocating odour, an alcohol was obtained by the above reaction, boiling at 112·5°, and having the composition $C_5H_{12}O$. This, on oxidation, yielded methyl-isopropyl-ketone; with phosphorus pentachloride, a chloride boiling between 86—87°; and with hydriodic acid, an iodide boiling at 127—129°. This alcohol possesses all the properties, which, according to Wischnegradsky, characterise methyl-isopropyl carbinol, and is consequently identical with it.

Kaschirsky seeks to interpret this singular reaction by means of the following analogy:—As is known, glycolic iodhydrin, treated with zinc-methyl, does not yield, as might be expected, normal propyl alcohol, but dimethyl carbinol. To this end, the product of the first stage of action, viz., $CH_2I.CH_2.OZnCH_3$, passes into ethene oxide, with separation of $Zn{<}^{I}_{CH_3}$, and the ethene oxide, at the moment of generation, isomerises into acetaldehyde, from which, by action of $Zn(CH_3)_2$, methyl-ethyl carbinol is obtained.

In this way, Kaschirsky supposes that $CH_2Br.CO.Br$ is first converted into $CH_2Br.C{<}^{OZnCH_3}_{(CH_3)_2}$, and that this compound passes over into $Zn{<}^{CH_3}_{Br}$, and into butylene oxide $(CH_3)_2{=}\overset{\ulcorner\!-O-\!\urcorner}{C-CH_2}$ which decomposes into isobutyl aldehyde, from which methyl-isopropyl carbinol is obtained. Butlerow interprets the above-mentioned reaction, also, in another way, viz., as follows:—

(1.) $CH_2Br{-}CO.Br + Zn(CH_3)_2 = CO{=}CHBr + Zn(CH_3)Br + CH_4$.
(2.) $CO{=}CHBr + CH_4 = CHBr(CH_3){-}CHO$.

The second stage may, also, be modified as follows:—It is possible that $CH.Br{:}CO$ may combine, not with $CH_3.H$ but with $Zn(CH_3)_2$, giving rise to an organic zinc-compound $(CH_3)BrCH{-}CO{-}Zn{-}CH_3$. Winogradoff has also obtained from zinc-ethyl and bromacetyl bromide, an alcoholic substance boiling at 165—166°. This substance has the composition $C_8H_{18}O$, and yields chlorides and iodides with PCl_5 and HI. If it be assumed that the action is the same as with zinc-methyl, then the alcohol $CH(C_2H_5)_2{-}C(C_2H_5)H(OH)$ must be formed.

W. S.

A Simple Method of Preparing certain Mono,- Di-, and Trichlorinated Acids. By E. DEMARÇAY (*Compt. rend.*, lxxxiv, 554—556).—This method consists in treating the substitution-products of acetyl-acetic ether, $CH_3CO.CH_2.CO.OC_2H_5$, with phosphoric chloride. If X and Y stand for alcohol-radicles, the reaction is this:—

$$CH_3.CO.CHX.CO.OC_2H_5 + PCl_5 = PCl_3O + HCl + CH_3CCl{=}CX.CO.OC_2H_5,$$

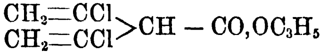
or the ether may have the formula—

$$CH_2{=}CCl - CHX.CO.O.C_2H_5.$$

By this means, the author has prepared *monochloromethyl-*, *ethyl-*, *propyl-*, *isopropyl-*, and *allyl-crotonic acids*.

If an ether of the formula $CH_3.CO.CXY.CO.OC_2H_5$ be treated with phosphoric chloride, it gives $CH_2{=}CCl—C(CH_3)_2—CO.OC_2H_5$. If the radicle X be acetyl, an acid, either identical or isomeric with dichlorosorbic acid, is obtained:—

$$(CH_3CO)_2{=}CH.CO.OC_2H_5 + 2PCl_5 + 2HCl + 2PCl_3O +$$



$$\left.\begin{matrix}CH_2{=}CCl\\CH_2{=}CCl\end{matrix}\right>CH - CO,OC_3H_5$$

If both the radicles, X and Y, are acetyl, the resulting product would belong to a series isomeric with the benzene series, and would have the formula:—

$$(CH_2{=}CCl)_3{\equiv}C—CO.OC_2H_5.$$

The author is about to attempt to carry out this reaction.

W. R.

On some Monochlorinated Acids of the Acrylic Acid Series. By E. DEMARÇAY (*Compt. rend.*, lxxxiv, 1087—1089).—These acids are prepared by the action of phosphorus pentachloride on the substitution-products of acetylacetic ethers. On adding the chloride, effervescence takes place, a red colour being produced on gently heating the mixture for some time. This coloration is due to the reaction of oxychloride of phosphorus upon the substitute of the acetylacetic ether.

When the action of the phosphorus pentachloride on the ether is finished, water is added to decompose the phosphorus oxychloride, a heavy oil being thus precipitated, which is the ether of the monochlorinated acid mixed with traces of free acid. The supernatant water also contains a certain proportion of this acid, which can be extracted by means of ether. This acid can generally be purified by distillation with aqueous vapour.

In the case of *monochloromethylcrotonic acid*, which is derived from acetylmethylacetic ether, an acid is distilled which crystallises in the cooled receiver. By fractional distillation an oily acid is produced towards the end of the operation, doubtless an isomeride of the solid acid. The same phenomena occur on purifying monochlorethylcrotonic acid. Monochloromethylcrotonic acid melts at 67° and boils from 209—210°, hardly undergoing decomposition. It dissolves in boiling water, and crystallises on cooling; its ethylic ether boils about 178—180°. By the action of alkalis in excess at a temperature of 140°, it is decomposed into carbon dioxide and monochlorobutylene.

Monochlorethylcrotonic acid, formed from acetyl-ethyl-acetic acid, melts at 74—75°, decomposing on boiling. At a temperature of 170° an effervescence commences, and at 240° nothing remains in the retort but a viscous mass containing very little acid. The product of distillation is a neutral body having an odour resembling that of monochlorobutylene, and absorbing bromine easily, most probably with formation of monochloramylene—

$$C_6H_9ClO_2 = CO_2 + C_5H_9Cl.$$

An acid isomeric with the preceding is easily prepared by means of dimethyl-acetyl-acetic ether. The chlorovinyl-dimethyl-acetic acid thus formed is purified by distillation with aqueous vapour; it crystallises in the clinorhombic system, and melts at 63—64°.

Chloroisopropylcrotonic acid has not been obtained in the liquid state. It crystallises at −25°, and cannot be distilled without decomposition, giving under these circumstances products analogous to those of monochlorethylcrotonic acid.

Monochloropropylcrotonic acid is a fluid oil with a repulsive odour, decomposing on distillation, and remaining liquid at − 28°. This acid, like the preceding, is easily attacked by bromine.

J. M. T.

Chlorinated Acrylic Acids. By O. WALLACH and P. HUNÄUS (*Deut. Chem. Ges. Ber.*, x, 567—570).—By the action of nascent hydrogen on chloralide, the authors have obtained the following, amongst other products:—

I. *Dichloracrylic Acid*, $CCl_2\equiv CHCO_2H$.—This acid crystallises from chloroform in needles or prisms, which dissolve sparingly in water, easily in ether and chloroform, melt at 77°, and volatilise readily.

The *ethyl ether*, $CCl_2CHCO_2C_2H_5$, is a strong-smelling liquid, boiling at 173—175°.

The *silver salt*, CCl_2CHCO_2Ag, forms white needles, which are moderately stable.

The *barium salt*, $(CCl_2CHCO_2)_2Ba + 5H_2O$, forms shining scales, easily soluble in water. The *calcium salt* closely resembles it.

The *potassium salt* forms highly refractive tables.

The *zinc salt*, $(CCl_2CHCO_2)_2Zn + 2H_2O$, consists of long compact crystals.

The *chloride*, $CCl_2CHCOCl$, formed by the action of phosphorus pentachloride on the free acid, boils above 145°, and yields with dry ammonia the *amide*, $CCl_2CHCONH_2$, which crystallises from chloroform in needles melting at 112—113°.

II. *Monochloracrylic Acid*, CClH – $CHCO_2H$.—This substance crystallises in laminæ which melt at 84—85°. Its *ethyl-ether* boils at 143—145°. The acid is identical with that obtained by Werigo and Werner from glyceric acid, and by Pinner from ethyl trichlorolactate.

J. R.

Conversion of Normal Pyrotartaric Acid into Dibromopyrotartaric and Dibromosuccinic Acids. By E. REBOUL and E. BOURGOIN (*Compt. rend.*, lxxxiv, 556—558).—By the action of 2 molecules of bromine on 1 molecule of pyrotartaric acid at 118—120° for nine hours, carbonic anhydride and hydrobromic acid are evolved, and dibromosuccinic acid is produced, showing that succinic acid and pyrotartaric acid are true homologues.

7·2 grams of normal pyrotartaric acid, when heated with 18 grams of bromine and 15 c.c. of water to 100° for 90 hours, gave some dibromosuccinic acid, dibromopyrotartaric acid, and an oily liquid which, after purification by washing with caustic potash, crystallised from a mixture of alcohol and ether in crystals melting at 54—55°. It was tetrabromethene hydride. A small quantity of another substance, melting at 45—46°, probably tetrabromo-propene, was also formed.

W. R.

Acetylenedicarbonic Acid. By E. BAUDROWSKY (*Deut. Chem Ges. Ber.*, x, 838—842).—When dibromo- or isodibromosuccinic acid is decomposed with an excess of alcoholic potash, a violent reaction takes place, and a little bromomaleic acid is formed, besides the chief product, which consists of *acetylenedicarbonic acid*, $C_4H_2O_4 . 2H_2O$, crystallising from ether in radiated masses, and losing their water over sulphuric acid. It begins to decompose at 100°, and at 180° the reaction is very violent: gases are given off, charcoal is left behind, and a few drops of a liquid smelling like acetic acid distils.

C_4O_4KH forms small glistening crystals dissolving sparingly in water. $C_4O_4Na_2 + 3\frac{1}{2}H_2O$ is precipitated by alcohol in fine silky needles. $C_4O_4Pb + H_2O$ is a precipitate consisting of silky crystals. The silver salt decomposes rapidly, even in the dark, explodes violently by percussion or heat; and the zinc salt crystallises in pyramids, consisting probably of $C_4O_4Zn + 1\frac{1}{2}H_2O$.

The anhydrous acid is isomeric with mellitic, and the crystallised with tartaric acid.

C. S.

Crotaconic Acid, a New Isomeride of Itaconic Acid. By A. CLAUS (*Deut. Chem. Ges. Ber.*, x, 822—824).—The acid which is formed by the action of potassium cyanide on ethyl chlorocrotonate is isomeric with the three pyrocitric acids, $C_3H_4(CO_2H)_2$, and may therefore be called *crotaconic acid*. To obtain free cyanocrotonic acid its potassium salt was decomposed with hydrochloric acid, and the solution exhausted with ether. On evaporation a mass remained which became crystalline on standing, and was no longer soluble in ether, consisting then of acid ammonium crotaconate. The free acid is very soluble in water, and does not crystallise well; it melts at about 119°, and is resolved at 130° into carbon dioxide and crotonic acid. By combining it with hydrobromic acid a new bromopyrotartaric acid is obtained, crystallising in long silky needles which melt at 141°. C. S.

The Volatile Acids of Croton-oil. By J. BERENDES (*Deut. Chem. Ges. Ber.*, x, 835—837).—Geuther and Fröhlich presume that the tiglic acid which they found in croton-oil was identical with Frankland and Duppa's methylcrotonic acid. The author has confirmed this statement. Both acids form plates having a peculiar smell like that of gum benzoïn, melting at 64°, and boiling at 196—197°. The calcium salts form small, foliated, warty masses, and contain 3 mols. of water; the barium salts are similar, but contain 4 mols. of water. The silver salts are white crystalline precipitates, and the two ethyl ethers boil at 154—156°. By fusing with potash the acids are resolved into acetic acid and propionic acid. Bromine converts them into a dibromovalerianic (dibromomethylethylacetic) acid melting at 82—83°; and hydriodic acid forms moniodovalerianic acid melting at 86·5°. They are not changed by the action of sodium-amalgam and water, but on heating them with hydriodic acid and phosphorus to 160°, methylethylacetic acid is formed boiling at 173—175°, and yielding an amorphous barium salt.

The higher-boiling portion of the volatile acids contains small quantities of higher homologues, one of which, $C_6H_{10}O_2$, boiling at 204°, was isolated. Of volatile fatty acids the following were found: formic, acetic, isobutyric, and common valerianic (isopropylacetic). The calcium salt of the latter forms with calcium tiglate a molecular compound crystallising in long needles. C. S.

Researches on the Synthesis of the Acids of the Series $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$ (Allyl- and Diallylacetic Acids). By E. REBOUL (*Compt. rend.*, lxxxiv, 1233—1236).—The successive action of sodium and ethyl iodide on acetic ether furnishes, according to Frankland and Duppa, four compounds, two of which are derived directly from a single molecule of ethyl acetate, and two others from double molecule minus one molecule of alcohol. Mixter, by the action of isybutyl iodide on the sodium derivatives of acetic ether, obtained only the two derivatives of the double molecule; and Zeidler showed that allyl iodide gave only allylic allylacetoacetate.

The author, by the action of allyl bromide on the sodium-derivatives of acetic ether, has obtained the four compounds corresponding with those obtained by Frankland and Duppa. Their proportion varies according to the quantity of sodium used. Their separation by fractional distillation is long and difficult, but they can be easily isolated by working in the following manner:—12 or 14 grams of sodium in thin slices are thrown into 160 to 170 grams of acetic ether free from water and alcohol, and kept boiling in a reflux apparatus until the sodium is completely dissolved, which takes place in four or five hours. The products of several operations are mixed and heated in a water-bath until the excess of acetic ether is driven off. The residue solidifies on cooling to a crystalline mass. It is decomposed by heating for eight or nine hours to 100° in closed vessels, with frequent agitation, after addition of a quantity of allyl bromide equivalent to the sodium dissolved. After cooling, the vessel is opened and water added, which separates a large quantity of oil, which is washed and distilled. The first portions consist of allylethylic ether and acetic ether; the principal portion passes over between 205—230 and is received apart; a smaller quantity comes over at a higher temperature, consisting mainly of ethylic diallylacetoacetate containing a small quantity of ethylic, allylacetoacetate.

The most abundant portion, passing over between 205—230°, consists of ethylic allylacetate, diallylacetate, allylacetoacetate, and diallylacetoacetate. It is placed in a flask with twice its weight of barium hydrate, and the flask is sealed and heated to 100° for nine or ten hours, with occasional agitation. The mass liquefies slowly and deposits barium carbonate. On heating in the oil-bath up to 200° (carefully, on account of bumping and frothing), water, alcohol, and allylacetone pass over, the last of which is separated by adding water to the distillate. The allylacetone, $CH_2(C_3H_5)—CO—CH_3$, is produced by the action of the baryta on the ethylic allylacetoacetate. The allyl- and diallylacetic ethers are saponified and converted into barium salts, which remain in the retort. They are dissolved in water, freed from baryta by carbonic acid, and evaporated.

Upon addition of dilute hydrochloric acid, the acids separate as an oily layer with a strong smell of valeric acid. They are washed, dried, and separated by fractional distillation.

Diallylacetic acid, $CH(C_3H_5)_2—CO_2H$, the most abundant of the two, is an oily liquid, of disagreeable odour, nearly insoluble in water. Sp. gr. 0·9578 at 13°. Boils at 224—226°. It dissolves with evolution of heat in alkaline liquids. The *silver salt*, $CH(C_3H_5)_2—CO_2Ag$, obtained by addition of silver nitrate to the potassium salt, forms light silky needles, moderately soluble in water. The *barium salt* crystallises well and contains two molecules of water of crystallisation. *Ethylic diallylacetate* is a light liquid, boiling at 195°. It is obtained by heating the acid with alcohol and sulphuric acid. If the acid be heated with alcohol and hydrochloric acid, the ether is mixed with chlorinated addition-products. Sodium-amalgam has no action on the acid.

Diallylacetic acid is produced, as the ethylic ether, by the action of allyl bromide on ethylic disodacetate—

$$CHNa_2—CO_2C_2H_5 + 2C_3H_5Br = CH(C_3H_5)_2—CO_2C_2H_5 + 2NaBr.$$

Ethylic mono- and diallylacetoacetate and allylacetone will be described in a future paper. C. W. W.

Some Derivatives of Acetylacetic Ether. By E. DEMARÇAY (*Compt. rend.*, lxxxiv, 1032—1033).—By the action of alcoholic potash on monobromated or on dibromated acetyl-isopropyl-acetic ether, two new acids are obtained approaching in composition to angelic and oxyangelic acids. Analysis of the first of these shows a composition corresponding with the formula $3C_6H_8O_2 . H_2O$. Although this substance does not yield crystallisable salts with any base, the author proposes to give it the name of *hexic acid.* The corresponding compound yielded by dibrominated acetyl-isopropyl-acetic ether he calls *hexenic* acid, its formula being $3C_6H_8O_3 . H_2O$. Similar compounds are also yielded by the homologues, acetyl-ethyl-acetic ether, and acetyl-methyl-acetic ether; and for these the several names of *pentic* and *pentenic*, *tetric* and *tetrenic acids* are proposed. R. R.

Thioglycollic Acid. By PETER CLAESSON (*Liebig's Annalen*, clxxxvii, 113—126).—By the action of monochloracetic acid on potassium sulphydrate, Carius obtained an acid of the formula $H.C_2H_2(HS)O_2$, which he called monosulphoglycollic acid. Some uncertainty was attached, however, to the constitution of the product of this reaction, and the author now shows that both thioglycollic acid, $H.C_2H_2(HS)O_2$, and thiodiglycollic acid, $H_2.(C_2H_2O_2)_2S$, are produced.

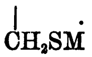
Thioglycollic acid, $H.C_2H_2.(HS)O_2$, is prepared by adding crystallised monochloracetic acid to a strongly concentrated solution of potassium sulphydrate in the proportion of one molecule to two. At the end of the reaction the product is concentrated on a water-bath, filtered, and the filtrate treated with excess of absolute alcohol. The filtered alcoholic solution is evaporated, the salt dissolved in water, and decomposed by sulphuric acid. Finally the acid is extracted with ether, and the ether evaporated off. Thioglycollic forms an uncrystallisable oil, completely soluble in water, alcohol, and ether, and having a faint odour. It is a strong acid, readily forming salts.

Potassium thioglycollate, $K.C_2H_2(HS)O_2 + H_2O$, formed by dissolving the acid in a solution of potassium carbonate, crystallises in masses of small needles, and is readily soluble in water and alcohol. Excess of alkaline carbonate converts it into a basic salt of the constitution $K.C_2H_2(KS)O_2$.

Barium thioglycollate, $Ba.(O_2H_2(HS)O_2)_2$. is a gummy mass readily soluble in water, but insoluble in alcohol.

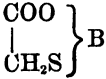
Ethyl thioglycollate, $C_2H_5.C_2H_2(HS)O_2$, formed by acting on a solution of thioglycollic acid in absolute alcohol with a few drops of concentrated sulphuric acid, is a highly offensively-smelling colourless oil, heavier than water, boiling with decomposition above 155°, and insoluble in alcohol and water.

Besides the normal salts, thioglycollic acid forms a series of salts of the form $M.C_2H_2(MS)O_2$ or



$\begin{array}{l}COOM\\ |\\ CH_2SM\end{array}$

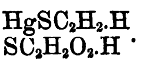
. The principal of these salts is the barium compound,



$\left.\begin{array}{l}COO\\ |\\ CH_2S\end{array}\right\}Ba$

$+ 3H_2O$, which is very characteristic. It is completely insoluble in cold water, and but slightly soluble in warm water. It can be formed by acting on the ordinary potassium thioglycollate with barium hydrate, or ammonia and barium chloride.

Mercurothioglycollic acid,



$\begin{array}{l}HgSC_2H_2.H\\ SC_2H_2O_2.H\end{array}$

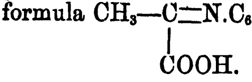
. This acid is obtained by the action of potassium thioglycollate on mercuric chloride, as an insoluble precipitate. It is soluble in boiling water and alcohol, and crystallises from the last either in long slender needles or short flat prisms. This new acid readily forms salts which are mostly crystalline. The barium salt, $\{Hg(SC_2H_2O_2)_2.H_2\}Ba$, crystallises in white microscopic crystals. The aluminium and manganese salts are similar in every respect. The lead salt, $\{Hg(SC_2H_2O_2)_2\}Pb$, is an amorphous precipitate obtained by adding mercurothioglycollic acid to a solution of lead acetate, and resembles the mercuric and silver salts.

Cuprosothioglycollic acid, $Cu_2.(SC_2H_2O_2)_2H_2$. is a whitish precipitate, formed by acting on a copper salt with excess of potassium thioglycollate. It dissolves in alkaline solutions forming salts. In a similar manner *bismuthothioglycollic acid*, $Bi(SC_2H_2O_2)_3H_3$, *argentothioglycollic acid*, $Ag.SC_2H_2O_2.H$, *plumboglycollic acid* and *cadmiumglycollic acid*, were obtained, together with some of their salts. E. N.

Leucine. By M. Nencki (*J. pr. Chem.* [2], xv, 390—398).—The author has prepared what he believes to be an isomeride of ordinary leucine, by the slow decomposition of albuminous bodies by means of pancreatic juice. The new leucine has a slightly sweetish taste; it is soluble in 43·6 parts of water at 14·5°; when heated in a test-tube, it sublimes at about 210° without fusion. The duration of the pancreatic fermentation materially affects the variety of leucine produced. If the process be stopped when the original acid reaction of the mixture has changed to neutral or slightly alkaline, the new variety of leucine is found to be present; but if the process be allowed to proceed for several days after this point has been reached, ordinary leucine is alone produced.

Pure egg-albumin yielded small quantities of ordinary leucine, by boiling with dilute sulphuric acid, no trace of the insoluble variety being produced. M. M. P. M.

Action of Aniline on Pyruvic Acid. By C. Böttinger (*Deut. Chem. Ges. Ber.*, x, 818—822).—The addition of pyruvic acid to an ethereal solution of aniline gives rise to an evolution of carbonic anhydride and heat, together with the separation of small lustrous crystals, which, however, separate only after long standing. These, when repeatedly washed with ether which is distinctly acid, dissolve in lukewarm water, leaving undissolved traces of a resinous body. The crystals, which are difficult to purify, even if purification is possible, owing to the persistent adherence of the above-mentioned resin, are of a pale yellow colour, changing to red at 114° and melting at 122°, at which temperature they froth, and melt to a brown liquid. The crystals, which have the composition $C_9H_9NO_2$, decompose when boiled with water, giving off carbonic anhydride; and the solution on evaporation yields white crystals, mixed with a small quantity of a brown substance. If the dried substance be heated, carbonic anhydride is disengaged in small quantities as well as water, the whole being converted, on cooling, into a hard resin, which melts in hot water, but remains insoluble. The same results are obtained when aniline is added to an aqueous solution of pyruvic acid, although the reaction takes place much more slowly. If pyruvic acid be regarded as a ketonic acid, the new acid may be represented by the formula



$$\begin{array}{l}CH_3{-}C{=}N.C_6H_5\\ \quad\;\;|\\ \quad\;\;COOH.\end{array}$$

E. W. P.

Observations on some Xanthates. Separation of Nickel and Cobalt. By T. L. Phipson (*Chem. News*, xxxv, 270).—Xanthate of potassium is easily prepared by means of alcohol, potash, and bisulphide of carbon; it crystallises easily, and may be kept in this state unaltered for an indefinite time in well-corked bottles. To use it as a reagent, a small quantity is dissolved for the occasion in cold distilled water. Xanthate of copper forms a brilliant orange-yellow precipitate when potassium xanthate is added to cupric salts, even very acid; it is a cupric salt. In neutral copper salts, or those which are slightly alkaline, a basic precipitate of a pale canary-yellow is produced. Xanthate of copper is almost completely insoluble in water, slightly soluble in alcohol, and rather more so in sulphide of carbon. Nitric acid attacks and dissolves it easily. When dry it burns like tinder, emitting a garlic odour, and on paper this combustion occurs with a fine purple flame, having a deep border of emerald green. It is quite insoluble in ammonia (the basic salt yields oxide). In this way xanthate of copper can easily be separated from other xanthates, which, on the contrary, are easily soluble in ammonia.

Xanthate of nickel forms a precipitate of a chocolate colour, almost insoluble in water, exceedingly soluble in ammonia. Xanthate of cobalt is a dark-green precipitate, almost insoluble in ammonia, which circumstance allows it to be easily and rapidly detected in nickel solutions, and separated from nickel. With certain precautions, this separation is quantitative. The two metals are precipitated together in the cold by solution of potassium xanthate, added gradually and whilst stirring, the liquid being made very slightly acid by hydrochloric acid. The precipitate is allowed to deposit completely, the supernatant liquid decanted off, and the nickel salt taken up by ammonia diluted with its own volume of water, which dissolves it instantaneously, leaving the xanthate of cobalt. Xanthate of zinc forms a brilliant white precipitate, very slightly soluble in water, much more so in alcohol and in sulphide of carbon, extremely soluble in ammonia. The ease with which xanthate of zinc dissolves in ammonia enables us to separate it rapidly and completely from the xanthates of lead, copper, cobalt, and indium. The solutions of nickel xanthate and zinc xanthate in dilute ammonia yield crystals of double ammoniacal salts by exposure to the air. In contact with excess of ammonia, these salts appear to undergo decomposition. The insoluble xanthate, on being dissolved in fuming nitric acid, previously diluted, develops nitrous ether, the odour of which is perceived the moment the solution commences. This proves, according to the author's view, that the xanthates contain a molecule of ethyl. D. B.

Cyanogen Compounds of Iron. By Z. H. Skraup (*Liebig's Annalen*, clxxxvii, 371—388).—Known quantities of titrated solutions of ferric chloride and potassium ferrocyanide were mixed; after standing for 24 hours, the supernatant liquors were poured off from the dark blue precipitates. When the solutions contained per c.c. 0·09043 Fe_2Cl_6 and 0·18674 $Fe_2Cy_{12}K_8$ respectively, and when quantities representing the ratios—

(1.) $Fe_2Cy_{12}K_8$ to Fe_2Cl_6
(2.) $3Fe_2Cy_{12}K_8$ to $4Fe_2Cl_6$
(3.) $7Fe_2Cy_{12}K_8$ to $8Fe_2Cl_6$
(4.) $2Fe_2Cy_{12}K_8$ to Fe_2Cl_6

were employed, the filtrates gave with ferric chloride blue precipitates in cases (3) and (4), and the same with ferrous sulphate; with ferrocyanide a precipitate was formed in case (2). The deep blue precipitates were readily soluble in water in each case save (2), when it was only partially soluble. Hence potassium ferricyanide was produced in cases (3) and (4); whilst in case (2) the iron was added in excess; in case (1) a very minute trace of ferricyanide was in solution. The precipitate obtained in this case was washed on a filter till the filtrate was blue, to remove any excess of potassium ferrocyanide, and was then dissolved in water and reprecipitated by potassium chloride; the slightly washed, drained, and vacuum-dried precipitate then gave on analysis numbers agreeing (after subtracting KCl) with the formula, $Fe_4Cy_{12}K_2.3\frac{1}{2}H_2O$.

A precipitate obtained from excess of potassium ferricyanide and ferrous sulphate free from ferric salt, was well washed by decantation with dilute potassium chloride solution, as free from air as possible, until all ferricyanide and sulphate were removed; no ferrocyanide was thus produced. The precipitate, after drying over sulphuric acid, gave numbers exactly agreeing with the above formula, and appeared to be in all respects identical with that previously obtained.

Soluble blue thus obtained gives, when in aqueous solution, a precipitate with both ferrous and ferric salts; potash decomposes these precipitates with formation of ferrocyanide in each case, ferrous oxide being formed in the first instance, ferric oxide in the second: the blue precipitate gave numbers agreeing roughly with $Fe_2Cy_{18}.15H_2O$.

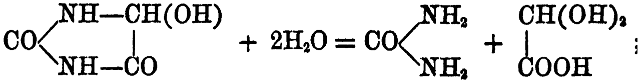
The author concludes from these experiments and the facts already known with reference to Prussian blue and Turnbull's blue, that soluble blue is the same whether prepared from a ferrous salt and a ferricyanide, or from a ferric salt and a ferrocyanide, and that when soluble blue is further acted on by an iron salt, the same product results, the action being, for the formation of soluble blue—

$$Fe_2Cy_{12}K_8 + Fe_2Cl_6 = 6KCl + Fe_2Cy_{12}K_2(Fe_2)$$
$$Fe_2Cy_{12}K_6 + Fe_2Cl_4 = 4KCl + Fe_2Cy_{12}K_2(Fe_2).$$

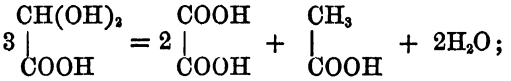
the only difference being that in the first formula the group (Fe_2) has the structure $\equiv Fe - Fe \equiv$, and the other Fe_2 group the structure $=Fe=Fe=$, whilst in the second formula these groups are reversed, which makes no difference to the molecules as a whole. Whether Prussian blue be formed by a ferrous or ferric compound acting on soluble blue, its production is always ultimately dependent on the exchange of Fe_2 for K_4, and the oxidation of the product, thus—

$$6Fe_4Cy_{24}Fe_4Fe_2 + 3O_2 = 8Fe_7Cy_{18} + 2Fe_2O_3.$$ C. R. A. W.

Decomposition of Glyoxalyl-urea. By L. Medicus (*Deut. Chem. Ges. Ber.*, x, 544—546).—Glyoxalylurea breaks up, under the action of potassium hydrate, in the manner indicated by the following equations:—



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NH{-}CH(OH)}\\ \quad\quad\ |\\ \mathrm{NH{-}CO}\end{array}\right. + 2\mathrm{H_2O} = \mathrm{CO}\left<\begin{array}{l}\mathrm{NH_2}\\ \mathrm{NH_2}\end{array}\right. + \begin{array}{l}\mathrm{CH(OH)_2}\\ |\\ \mathrm{COOH}\end{array};$$

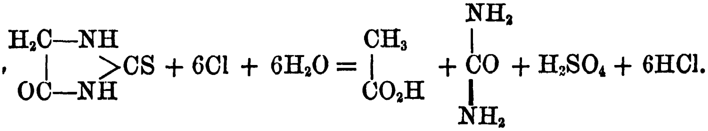


$$3\begin{array}{l}\mathrm{CH(OH)_2}\\ |\\ \mathrm{COOH}\end{array} = 2\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{COOH}\end{array} + 2\mathrm{H_2O};$$

the ultimate products being ammonia, acetic acid, and oxalic acid.

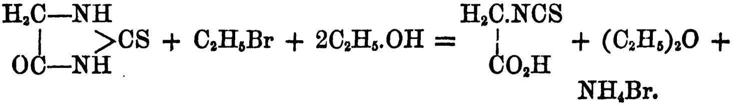
J. R.

Thiohydantoïn. By A. Claus (*Deut. Chem. Ges. Ber.*, x, 324—327).—As thio-carbamide (sulphurea) combines with the halogens, it appeared of interest to see whether thiohydantoïn, which is regarded as a substitution-product of thio-carbamide, would form similar additive products. But this is not the case, chlorine decomposing the hydantoïn at a low temperature in the following way:—



$$\begin{array}{l}\mathrm{H_2C{-}NH}\\ |\\ \mathrm{OC{-}NH}\end{array}\!\!>\mathrm{CS} + 6\mathrm{Cl} + 6\mathrm{H_2O} = \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CO_2H}\end{array} + \begin{array}{l}\mathrm{NH_2}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NH_2}\end{array} + \mathrm{H_2SO_4} + 6\mathrm{HCl}.$$

Bromine acts in a similar manner, but as the reaction went on at the common temperature, the carbamide was resolved into ammonia and carbon dioxide. When thio-hydantoïn is heated with ethyl bromide and alcohol to 130—140°, no additive compound is formed, but the ethylic ether of Volhard's thio-carbimidacetic acid:—



$$\begin{array}{l}\mathrm{H_2C{-}NH}\\ |\\ \mathrm{OC{-}NH}\end{array}\!\!>\mathrm{CS} + \mathrm{C_2H_5Br} + 2\mathrm{C_2H_5.OH} = \begin{array}{l}\mathrm{H_2C.NCS}\\ |\\ \mathrm{CO_2H}\end{array} + (\mathrm{C_2H_5})_2\mathrm{O} + \mathrm{NH_4Br}.$$

On heating thiohydantoïn with alcoholic ammonia to about 130°, glycolamide, $CH_2(NH_2).CO(NH_2)$, is formed, which is partly decomposed with formation of ammonium carbonate.

C. S.

New Method of Brominating Aromatic Hydrocarbons in Presence of Aluminium Bromide. By G. Gustavson (*Deut. Chem. Ges. Ber.*, x, 971).—When bromine acts on benzene, toluene, or mesitylene, and probably also on naphthalene, in presence of aluminium bromide, the action is very energetic, and requires moderating by carefully cooling the vessel; if the hydrocarbon be added to excess of bromine containing the bromide in small quantities, the whole of the hydrogen in the aromatic nucleus (but not in the lateral chains) is replaced by bromine, even at 0°; if the bromine solution be added to the hydrocarbon, the bromination can be stopped at any desired point by simply regulating the quantity added. C_6Br_6 was thus readily obtained from benzene (Gessner prepared it by acting on benzene with bromine containing iodine for 150 hours, at 350—400°); mesitylene, however, formed only *tri*bromomesitylene, $C_9H_9Br_3$, identical with that of Fittig and Storer, whilst toluene produced $C_7H_5Br_3$ on treatment with quantities of bromine sufficient to replace all the hydrogen present, no further replacement being practicable, even on heating with excess of bromine and aluminium bromide. Naphthalene gives a bromoderivative, crystallising in fine needles, like glass wool, and melting at a higher temperature than Gessner's hexbromonaphthalene. Hence the process appears likely to furnish, not only a convenient method for brominating organic bodies, but also a means of determining their nature and structure. C. R. A. W.

Derivatives of the Xylenes. By O. JACOBSEN (*Deut. Chem. Ges. Ber.* x, 1014—1015).—Metaxylenesulphonic amide was obtained in two modifications, the first, which is identical with one described by Witting and Post, crystallises from alcohol in large, pearly plates, and from water in very long needles, melting at 137°. The second amide crystallises from water in flat, flexible needles, and from alcohol in needles or more compact crystals, which are grouped in rosettes, and melt at 95—96°. An amide melting at 123°, which Witting and Post describe, could not be obtained. When the first amide is heated with hydrochloric acid to 145—155°, the sulphonic acid is formed, while above 160° the hydrocarbon separates out.

Paraxylenol forms crystals melting at 74·5°, and boiling at 210—211°, and orthoxylenol melts at 61°, and boils at 223—225°.

C. S.

Preparation of Paraxylene from Coal-tar Oil. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, 1009—1010).—When crude coal-tar xylene is shaken with warm common sulphuric acid, only traces of paraxylene are dissolved. After treating the insoluble portion several times in this way, and then shaking it with warm, slightly fuming acid, paraxylene-sulphonic acid is formed, while a paraffin boiling at 150° is left behind. The sulphonic acid forms a hydrate, $C_8H_9.SO_3H + 2H_2O$, which is very sparingly soluble in dilute sulphuric acid, and crystallises in large prisms or plates. It may be purified by crystallisation, or by converting it into the barium- or sodium-salt. The barium-salt $(C_8H_9CO_3)_2Ba$, crystallises in presence of traces of its isomerides in opaque white crusts, but when pure in glistening scales, or more compact transparent crystals. 100 parts of water dissolve at 0°, 2·27, and at 100°, 5·53 parts of the salt. The sodium $C_8H_9SO_3Na + H_2O$ forms flat, striated prisms. On subjecting this salt or the free acid to dry distillation, or heating them with hydrochloric acid to 195°, pure paraxylene is obtained, which crystallises on cooling, and does not melt completely at 14·5°. C. S.

Occurrence of Orthoxylene in Coal-tar. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, x, 1009—1014).—The portion of crude xylene which is soluble in common sulphuric acid is a mixture of the meta- and ortho-compound. To separate these, the sulphonic acids were converted by Otto and Schiller's method into the sulphinic acids, which formed a liquid mixture. On converting them into the sodium salts, and concentrating the solution, sodium orthoxylenesulphinate crystallises out first in long prisms, which are easily purified by recrystallisation. On adding an acid to its warm or concentrated solution, otho-xylenesulphonic acid separates as an oil, which soon solidifies, and crystallises from warm water in large, thin, silky plates, melting at 83°. On triturating it under water with pure barium peroxide, barium orthoxylenesulphonate is formed, crystallising in large, pearly, rhombic plates, containing 1 mol. of water. 100 parts of water dissolve at 0°, 5·8, and at 100°, 33·6 parts of the crystallised salt.

$C_8H_9SO_3Na + 5H_2O$ crystallises exceedingly well in long, flat prisms. Orthoxylenesulphonic *chloride* separates from ether in very large, prismatic crystals, melting at 51—52°, and the *amide* crystallises from alcohol in prisms, melting at 144°. On heating it or the sodium salt with hydrochloric acid to 190—195°, pure orthoxylene, boiling at 142—143°, is obtained. With a mixture of nitric and sulphuric acid it yields first a liquid and then a solid nitro-compound, which after repeated crystallisation from alcohol, melts at 52—55°. A hot solution of potassium permanganate oxidises it to orthotoluic and phthalic acids.

The mother-liquors of sodium orthoxylenesulphinate contain the salts of the two metaxylenesulphinic acids, which are precipitated by acids as an oily liquid, crystallising after a short time. On crystallising them from alcohol, products melting between 42° and 50° were obtained. By means of barium peroxide they were converted into the barium sulphonates, which on evaporation crystallised in hard crusts, or semi-globular masses, consisting of small, pointed crystals containing 1 mol. of water. 100 parts of water dissolve at 0°, 9·5—10·3, and at 100°, 14·3—15·9 parts of the salts of different crystallisations. Whether the two sulphonates form a double salt or are a mixture must be decided by future experiments.

The coal-tar oils which were examined contained all the three xylenes, 20—25 per cent. of the latter consisting of the para-, and 10—15 of the ortho-compound. To separate them, the crude xylene is shaken with common sulphuric acid, and the insoluble portion used for the preparation of paraxylene, as already described. The acid solution is neutralised with chalk, the filtrate mixed with a slight excess of sodium carbonate, and concentrated, until on cooling a considerable quantity of sodium orthoxylenesulphonate crystallises out, which is obtained pure by pressing and 2 or 3 recrystallisations. As soon as on further concentration of the mother-liquor, no more distinct crystals are obtained, the solution contains only the metasulphonate. C. S.

Sulphuretted Derivatives of Cymene. By J. BERGER (*Deut. Chem. Ges. Ber.*, x, 976).—Alcoholic ammonia and the chloride of cymene-sulphonic acid form *cymene-sulphamide*, $C_{10}H_{13}.SO_2.NH_2$, melting at 110°; when dissolved in boiling water, this substance forms

with silver acetate a precipitate consisting of $C_{10}H_{13}.SO_2.NHAg$. The chloride of the sulphonic acid yields by treatment with zinc dust and water, the zinc salt of *cymenesulphinic acid*, $C_{10}H_{13}.SO_2H$. The acid itself is obtained by decomposing the zinc salt with sodium carbonate, &c., setting free the acid by hydrochloric acid, and agitating with ether; it forms a bright yellow syrup, but little soluble; its copper, silver, lead, and potassium salts have been prepared, the first three being obtained as precipitates, the last as crystals containing $C_{10}H_{13}.SO_2K$, $3\frac{1}{2}H_2O$; the silver-salt treated with ethyl and propyl iodide gave syrupy ethers, which could not be purified by distillation, owing to decomposition.
C. R. A. W.

Preparation of Aromatic Nitrils. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 746).—When chlorobenzene is passed over a mixture of ferrocyanide of potassium and quartz-sand at a dull red heat, the reaction $C_6H_5Cl + KCN = KCl + C_6H_5.CN$ takes place to a small extent, *benzonitril* being formed boiling at 191° and forming benzoic acid on saponification; at a higher temperature carbonisation ensues to a considerable extent and ammonium cyanide and benzene are formed. Bromobenzene acts similarly, whilst dibromobenzene produces ultimately a little terephthalic and benzoic acids. Chlorotoluene forms ortho- and paratoluic acids (from the corresponding modifications of the chlorotoluene employed): the ortho-acid melted at 102° and formed phthalic acid on oxidation by permanganate. Bromonaphthalene forms at a dull red heat only a little α-naphthyl cyanide, a much better yield being obtained at a higher temperature; on heating with hydrochloric acid to 180° this compound yields *α-naphthoic acid* in quantity, so that this form of reaction affords a convenient mode of preparing that acid. The monosulphonic acids and monobrominated derivatives of naphthalene, benzene, and toluene exhibit a certain analogy in the relative facility with which they are convertible into nitrils, the two naphthalene compounds affording the largest yield of nitril, the benzene-compounds a smaller yield, and the toluene-compounds the smallest of all.

When chlorobenzene is heated to 300—400° in sealed tubes with excess of various metallic cyanides for several hours benzonitril is often formed; only a slight pressure is usually noticeable on opening the tubes, ammonia, hydrocyanic acid, and sometimes cyanogen gas being formed, the former apparently only when a little moisture has been present. Ferrocyanide of potassium thus treated yielded in ten hours about 20 per cent. of the theoretical amount of benzoic acid. and with bromobenzene it produced about 22 per cent.; crystallised bromotoluene formed only small quantities of toluic acid melting at 177°. Lead cyanide acted less energetically on chlorobenzene, bromobenzene, bromotoluene, and bromonaphthalene, forming in each case small quantities of the respective nitrils; silver cyanide formed only traces of benzoic and α-naphthoic acid after saponification of the products. When, however, iodobenzene and iodotoluene were employed, silver cyanide gave rise to much larger amounts, as also did iodonaphthalene; ortho-iodotoluene acts more readily than para-iodotoluene, whilst iodonaphthalene (from mercury-dinaphthyl and iodine dissolved in carbon disulphide) gives rise to a naphthoic acid melting at 142—143° even after purification by frequent recrystallisation, and conversion into calcium salt. The authors regard this acid as a "physical isomeride" of α-naphthoic acid melting at 160°.

On heating benzene and mercuric cyanide for ten hours to 300—350°, benzonitril was formed, yielding benzoic acid on saponification; similarly α-naphthoic acid was obtained from naphthalene. Larger quantities of benzoic acid were obtained by passing a slow stream of cyanogen gas through gently boiling benzene and then through a tube heated to low redness; a little terephthalic acid and a small quantity of a substance agreeing in physical characters with isophthalic acid was also obtained, together with a little diphenyl melting at 70°. Naphthalene yielded α-naphthoic acid without admixture of the β-acid by this mode of treatment.

Cyanogen bromide and benzene react on one another at 200—240°, forming bromobenzene and hydrocyanic acid, but no benzonitril. Analogous results were obtained with naphthalene. Similarly on heating dimethyl-aniline and cyanogen iodide, *dimethyl-iodaniline*, $N(CH_3)_2.C_6H_4I$, was obtained melting at 79°. Hence whilst the halogen substitution-products of aromatic hydrocarbons will react with metallic cyanides, and the hydrocarbons themselves with cyanogen gas, to form nitrils, these latter bodies are not formed by the action of cyanogen derivatives on the hydrocarbons. C. R. A. W.

Derivatives of Dimethylaniline. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 760).—Dimethylaniline is oxidized by fuming nitric acid too rapidly to form a nitro-derivative, but if it be dissolved in 10 or 12 parts of glacial acetic acid, and the calculated amount of acid gradually added, there is obtained, after cooling and standing, crystalline *mononitrodimethylaniline*, melting at 163°, after crystallisation from alcohol and benzene; this body does not form salts nor even a platinochloride. Heating with soda-solution in various ways did not produce any splitting up into nitrophenol and dimethylamine (nitrosodimethylaniline thus treated forms nitrosophenol and dimethylamine—Berger and Caro). Hydrochloric acid at 180° eliminated methyl as chloride, but the complementary product (presumably nitraniline) was decomposed. Reduction by tin and hydrochloric acid formed *amidodimethylaniline* which gives rise to the compound—

$$C_6H_4(NH_2).N(CH_3)_2,2HCl,SnCl_2,$$

crystallisable from alcohol, and forms methyl-chloride and paraphenylenediamine on heating with hydrochloric acid to 180—200°; this diamine melted at 139°, and readily formed quinone on oxidation with manganese dioxide and sulphuric acid or with ferric chloride. By the action of nitric acid on mononitrodimethylaniline dissolved in glacial acetic acid, the dinitro-derivative is formed, melting at 77°.

Bromine added cautiously to dimethylaniline dissolved in glacial acetic acid, forms *monobromodimethylaniline* melting at 55°, and distillable at 247°. The salts of this body are very soluble and deliquescent; apparently therefore this is the meta-derivative obtained by Wurster and Grubemann from bromonitrobenzene. Iodine dissolved in carbon disulphide forms iododimethylaniline, on addition to methylaniline dissolved in the same liquid. This base melts at 79°, and when heated for a moment above its melting point, forms a substance soluble in alcohol, with beautiful violet colour, presenting great similarity to Poirier's "methyl violet." This body may probably be formed by the reaction—

$$3[C_6H_4I.N(CH_3)_2] = 3HI + C_{24}H_{27}N_3.$$

C. R. A. W.

Action of Hydrogen Sulphide on the Isonitrils. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, x, 1095—1098).—When phenyl isocyanide is placed in a large vessel filled with hydrogen sulphide, it becomes transformed in the course of a few days into a crystalline mass of *thioformanilide* or *phenylthioformamide*, which may at once be obtained in the pure state by dissolving it out with ether and crystallisation from boiling water. As, however, it is troublesome to prepare the isocyanide in the pure state, an attempt was made to obtain the thioformanilide from the crude product of the action of chloroform on aniline in presence of an alcoholic solution of potash. It was found that by mixing this with a saturated alcoholic solution of potassium sulphide, and leaving it for some hours, a considerable quantity of the anilide was formed along with other substances. On pouring the alcoholic solution into water, an oil was deposited, containing—besides the thioformanilide—phenylisocyanide, methyldiphenyldiamine, and unaltered aniline and chloroform. It was therefore treated with hydrochloric acid to remove aniline, and the residue, after exposure to the air to allow the chloroform to evaporate, was dissolved in boiling water, and filtered. On cooling, the thioformanilide crystallised out, whilst the methenyldiphenyldiamine remained in solution as hydrochloride. Pure thioformanilide crystallises in long, colourless needles which melt at 137·5° with partial decomposition, splitting up into phenyl isocyanide and hydrogen sulphide: $C_6H_5.NH(CSH) = C_6H_5.NC + SH_2$. Its aqueous solution is intensely and persistently bitter. It dissolves readily in cold dilute alkaline solutions, and is precipitated unchanged on the addition of an acid; but on heating the alkaline solution, the thio-compound is decomposed, with formation of an alkaline sulphide and formate, and liberation of aniline.

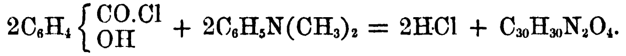
Thioformanilide, $C_6H_5.NH(CSH)'''$, bears the same relation to the isomeric thiobenzamide, $C_6H_5.C(HS).NH_2$, that the isonitril, $C_6H_5.N{\equiv}C$, does to the nitril, $C_6H_5.C{\equiv}N$. C. E. G.

Preparation of Monomethylaniline, and Experiments on the Action of Methyl Chloride, Bromide, and Iodide on Aniline. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, x, 588—601).—In a recent paper by Kern it was stated by that chemist, as the result of his experiments, that in the action of methyl chloride, bromide, or iodide on aniline, no monomethylaniline is formed, the product being in all cases dimethylaniline only. The author of the present paper severely criticises Kern's conclusion, and shows it to be utterly erroneous. He has investigated the action of methyl chloride, bromide, and iodide on aniline, and finds that the dimethylaniline produced in the reaction is invariably accompanied by a considerable quantity of the monomethyl-compound, the proportion of the latter being greatest when methyl chloride is employed.

Thus methyl chloride acting upon aniline in excess produced dimethylaniline and monomethylaniline in the proportion of 4 : 3; methyl bromide under like conditions produced the same products in the proportion of 3·3 : 1, whilst with methyl iodide these products were in the proportion of 4·2 : 1.

Monomethylaniline is readily separated from the dimethyl-compound by means of acetic anhydride, which reacts with the former to produce crystalline methylacetanilide, but has no action on the latter. J. R.

Saliceïn of Methylaniline. By Otto Fischer (*Deut. Chem. Ges. Ber.*, x, 954).—When salicyl chloride and dimethylaniline are made to react on one another, minute quantities of zinc-dust being added, a phthaleïn-like body is formed apparently in virtue of the reaction,



$$2C_6H_4\left\{\begin{matrix}CO.Cl\\OH\end{matrix}\right. + 2C_6H_5N(CH_3)_2 = 2HCl + C_{30}H_{30}N_2O_4.$$

The hydrochloride of this base $C_{30}H_{30}N_2O_4.HCl.2H_2O$ (after drying at 110°) may be obtained, as a flocculent precipitate, by washing with water, solution in hydrochloric acid, precipitation by large addition of water, and finally solution in chloroform and precipitation with ether. It dyes silk much like methyl green, and is of much higher tinctorial power than methylaniline phthaleïn. It forms two platinum salts, $C_{30}H_{30}N_2O_4.2HCl_2.PtCl_4$ and $2(C_{30}H_{30}N_2O_4.HCl).PtCl_4$. The acetate, sulphate, nitrate, and oxalate are obtainable by adding to the solution of the hydrochloride in dilute potash the appropriate acid, and purifying the precipitates by solution in chloroform and precipitation with ether. Melting caustic potash reproduces salicylic acid and dimethylaniline; zinc-dust and glacial acetic acid reduce it to a colourless body. Bromine gives a colourless bromo-derivative, acetic anhydride a bright yellow acetyl-derivative, and fuming nitric acid a yellow nitro-compound. Analogous green colouring matters are formed with salicyl chloride and diethylaniline, and methyl-diphenylamine. C. R. A. W.

Nitro-compounds of Dimethylaniline. By K. Mertens (*Deut. Chem. Ges. Ber.*, x, 995—996).—On leaving a mixture of 10 parts of dimethylaniline, 110 of nitric acid, and 110 of water to stand for six hours, a dinitrodimethylaniline is formed, separating from benzene in splendid crystals melting at 87°. Caustic potash resolves it into pure dimethylamine and α-dinitrophenol melting at 114°. Dinitrodimethylaniline hydrochloride exists only in solution, and forms a well-crystallising platinochloride, which may be recrystallised from hydrochloric acid containing platinic chloride. An isomeric dinitrodimethylaniline, which is formed but in small quantity at the same time, is insoluble in alcohol, but dissolves in glacial acetic acid and

high-boiling benzene, and melts under decomposition at 240—260°. Boiling nitric acid converts dimethylaniline into a pale-yellow crystalline compound, melting at 127°. Its alcoholic solution is coloured reddish-brown by caustic potash, and on boiling it with aqueous potash, it yields ammonia, probably dimethylamine, and potassium picrate and nitrite.
C. S.

Benzoyl-dimethylaniline. By OTTO FISCHER (*Deut. Chem. Ges. Ber.*, x, 958).—By heating to 180—200° for 6—8 hours, a mixture of phosphoric anhydride, benzoic acid, and dimethylaniline, benzoyl-dimethylaniline, $C_6H_5.CO.C_6H_4.N(CH_3)_2$, is formed, boiling at 330—335°, crystallising on standing, melting at 38° after purification by shaking its ethereal solution successively with alkali and acid, and crystallising from petroleum ether. It is destitute of basic properties; with nitric acid it gives a crystallised dinitro-derivative, melting at 142°, and with bromine a crystalline bromo-derivative.
C. R. A. W.

Triethylbenzylammonium Iodide. By VICTOR MEYER (*Deut. Chem. Ges. Ber.*, x, 964).—The author maintains, in opposition to Ladenburg, that the bodies formed by adding benzyl iodide to triethylamine, and ethyl iodide to benzyl-diethylamine, are absolutely identical. Ladenburg suggests that the one isomeride is convertible into the other under certain circumstances; the author finds no difference under any circumstances. When pure, neither gives off benzyl iodide on heating with hydriodic acid, although impure preparations give off minute amounts. To prevent misconception, he describes in detail the exact mode of manipulation adopted in the experiments, the results of which have already appeared (*Berichte*, x, 309; and p. 190 of this volume).
C. R. A. W.

On the Base, $C_{13}H_{13}N$, from Aniline Tailings. By C. LORING JACKSON (*Deut. Chem. Ges. Ber.*, x, 960).—The author concludes that this base is not identical with that which Carnelley obtained by reducing nitrotolylphenyl. The two preparations melt at 47·5° and at 93—97° respectively, and form very different hydrochlorides, melting at 280—283° and 200° respectively. The aniline base gives a characteristically crystallised platinum salt, which was not observed by Carnelley.
C. R. A. W.

Aniline-black Dye-bath. Transformation of Aniline-black into a Fluorescent Rose-coloured Substance. By FR. GOPPELSROEDER (*Compt. rend.*, lxxxiv, 447—450).—The base of electrolytically-prepared aniline-black is soluble in fuming sulphuric acid, and the solution, when poured into water, furnishes a green precipitate, which dissolves, after washing, in pure water. The addition of an alkali to this solution turns it blue, but the green colour is restored by acids. It is decolorised by nascent hydrogen, and assumes various shades of colour, blue, violet, yellow, &c., when treated with different chemical reagents. The blue alkaline solution may be used as a dye-bath after decolorisation with reducing agents, since the colour returns when the materials are exposed to the air. Its most important use, however, is for dyeing black, which is effected by oxidising the colour with an acid solution of ferric chloride, after it has been fixed upon the fibre as before mentioned. This black is not turned green by acids, but may be associated with the usual indigo-vat if required.

The analysis of the base leads to the formula $C_{24}H_{20}N_4$, which the author regards as a sort of tetrazobenzene $(C_6H_5N)_4$. The colourless and coloured compounds (other than black) of this base are therefore hydrogen-derivatives; while the black is probably an oxidised derivative of the same. The base of this aniline-black, when fused with acid potassium sulphate, evolves sulphurous oxide and nitrogen, leaving a mass which is only partially soluble in cold water. The insoluble residue dissolves in hot concentrated sulphuric acid, from which it is reprecipitated on the addition of water. This precipitate, which is black, yields to alcohol a highly fluorescent rose-coloured substance, which possesses the same spectral and chemical reactions as naphthalene-red. Moreover, it dyes silk in a similar manner to, and of the same colour, as the naphthalene-compound. Its composition has not yet been ascertained. J. W.

The Phthaleïns of Tertiary Aromatic Bases. By Otto Fischer (*Deut. Chem. Ges. Ber.*, x, 952).—The phthalin of dimethylaniline is obtained by the process formerly described by the author, viz., reduction of the phthaleïn with zinc-dust and glacial acetic acid, and is then purified by crystallisation from wood spirit; it is readily soluble in alcohol and ether, and has the composition $C_{24}H_{26}N_2O_3$, or, $C_6H_4\begin{cases} CH.(OH)C_6H_4.N(CH_3)_2 \\ CO.C_6H_4.N(CH_3)_2 \end{cases}$. The picrate is thrown down as a bright yellow precipitate on mixing ethereal solutions of the base and of picric acid; the platinum salt is nearly colourless.

The phthaleïn, heated considerably above 200° with melting potash, produces phthalic acid and dimethylaniline. Fuming nitric acid converts the phthaleïn into a hexnitro-compound $C_{14}H_{18}(NO_2)_6O_2$.

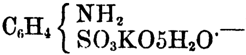
C. R. A. W.

Action of Nitrous Acid on substituted Amides. By Otto Fischer (*Deut. Chem. Ges. Ber.*, x, 959).—By acting on acetoparatoluide with nitrous acid, *nitrosoacetoparatoluide*,—

$$C_6H_4(CH_3).N(NO).C_2H_3O,$$

is obtained, melting at 80°, with decomposition; readily soluble in ether, alcohol, benzene, chloroform, and glacial acetic acid. Benzanilide does not undergo any analogous change, but formanilide gives rise to *nitrosoformanilide*, $C_6H_5.N(NO).COH$, melting at about 39°. Similarly, oxanilide produces *nitrosoxanilide*, $C_6H_5.NH.CO.CO.N(NO).C_6H_5$, melting at 86°. All these bodies are yellowish, puff up when heated, and give Liebermann's reaction with phenol and sulphuric acid They are not reducible to hydrazins. C. R. A. W.

On Orthamidobenzenesulphonic, Orthobromobenzenesulphonic Acids, &c. By AD. BAHLMANN (*Liebig's Annalen*, clxxxvi, 307—326).—In addition to the results of Berndsen and Limpricht (*Annalen*, clxxvii, 98; this Journal, 1875, p. 1029), the author has prepared the two following salts:—

Potassium orthoamidobenzenesulphonate,  $C_6H_4\left\{\begin{matrix}NH_2\\SO_3KO5H_2O\end{matrix}\right.$—Large, colourless, well formed prisms, easily soluble in water.

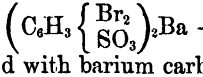
Silver orthoamidobenzenesulphonate, $C_6H_4\left\{\begin{matrix}NH_2\\SO_3Ag\end{matrix}\right.$—Anhydrous, consisting of slender brittle, brownish needles, easily soluble in hot water, the solution becoming dark red when heated.

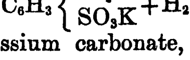
The action of bromine on orthoamidobenzenesulphonic acid gives rise to the formation of sulphuric acid, tribromaniline, monobromamidobenzenesulphonic, and dibromamidobenzenesulphonic acids.

The last-named acid may be represented by the formula—$SO_3H : NH_2 : Br : Br = 1 : 2 : 3 : 5$.

Monobromamidobenzesulphonic acid is prepared by adding drop by drop one molecule of bromine to a very dilute cold solution of barium orthamidobenzenesulphonate. The colour of the bromine disappears, and a precipitate of tribromaniline and barium sulphate is thrown down. The liquid is heated to boiling, neutralised with barium carbonate, and filtered hot. On evaporation, barium dibromamidobenzenesulphonate first crystallises out, next barium monobromamidobenzenesulphonate, and, finally, barium amidobenzenesulphonate and barium bromide. The monobromamido-acid is best separated from the amido-acid by stirring them with water at 60 to 70°, pouring off the liquid from the undissolved amido-acid, and filtering at about 30°,

Monobromamidobenzenesulphonic acid crystallises in long, white, silky needles, which are soluble in hot water, but not in alcohol. When heated on platinum foil they are carbonised, without previously melting. The diazo-compound is formed by acting on the finely divided acid (suspended in cold alcohol) with nitrous acid. It consists of small hexagonal plates which dissolve, with the aid of heat, in water and alcohol, with evolution of nitrogen. They explode when heated or struck. On treatment with warm concentrated hydrobromic acid, they dissolve with evolution of gas, and on evaporation leave a crystalline residue of *paradibromobenzenesulphonic acid*—$SO_3H : Br : Br = 1 : 2 : 5$, which forms hydrated crystals melting at 97°.

Barium dibromobenzenesulphonate,  $\left(C_6H_3\left\{\begin{matrix}Br_2\\SO_3\end{matrix}\right.\right)_2Ba$ + 2 and $3H_2O$, prepared by neutralising the free acid with barium carbonate, crystallises in white plates, or in dense transparent prisms, at times, also in warty masses. When the acid was converted into the chloride, and this again into the acid, the barium salt was found to be less soluble. It consisted in that case of brilliant white needles, containing one molecule of water.

Potassium dibromobenzenesulphonate,  $C_6H_3\left\{\begin{matrix}Br_2\\SO_3K\end{matrix}\right.+H_2O$, prepared from the barium salt by means of potassium carbonate, consists of tufts of acicular crystals.

Dibromobenzenesulphochloride, $C_6H_3\left\{\begin{matrix}Br_2\\SO_2Cl\end{matrix}\right.$, forms well-shaped, solid crystals, which melt at 71°.

Dibromobenzenesulphamide, $C_6H_3\left\{\begin{matrix}Br_2\\SO_2NH_2\end{matrix}\right.$, consists of brittle, feathery needles, melting at 192—193°.

From the above facts there is no doubt that the structure of the dibromo-acid is $SO_3H : Br : Br = 1 : 2 : 5$ and that of the amidobromo-acid $SO_3H : NH_2 : Br = 1 : 2 : 5$.

Thomas obtained the same *amidobromobenzenesulphonic acid* (*Annalen*, clxxxvi, 123) from metabromobenzenesulphonic acid, and since, when heated with hydriodic acid and phosphorus, it passes into orthamidobenzenesulphonic acid, it is possible to obtain this latter body by starting from metabromobenzenesulphonic acid.

The action of bromine on orthamidobenzenesulphonic acid may be considered to be definitely settled as giving rise, first to $SO_3H : NH : Br = 1 : 2 : 5$, and, secondly, to $SO_3H : NH_2 : Br : Br = 1 : 2 : 3 : 5$.

Orthobromobenzenesulphonic Acid.—The properties, salts, &c., of this acid have already been described (*Annalen*, clxxxi, 203). When acted on by very concentrated nitric acid it gives rise to two nitrobromobenzenesulphonic acids, which may be separated by repeated crystallisation of the barium salts. The first of these, *nitrobromobenzenesulphonic acid*, $SO_3H : Br : NO_2 = 1 : 2 : 5$, $2H_2O$, consists of large flat prisms, of a faint yellow colour, which are very soluble in water and alcohol. They slowly lose their water of crystallisation, without melting, at 110°, but at 130—135° they melt, and part with it quickly.

The ammonium, potassium, and sodium salts all consist of fine white easily soluble needles, and are anhydrous. The barium salt crystallises with five molecules of water in white silky needles, easily soluble in hot water. The calcium salt contains four molecules, and the zinc salt seven molecules of water; both are easily soluble. The silver salt is anhydrous, less soluble, and becomes dark coloured when exposed to the light.

Nitrobromobenzenesulphochloride crystallises in large rhombic plates, which melt at 92°.

Nitrobromobenzenesulphamide consists of slender white needles, melting at 205°.

Amidobromobenzenesulphonic acid, $SO_3H : Br : NH_2 = 1 : 2 : 5$, $2H_2O$, prepared from the nitro-acid by the action of tin and hydrochloric acid, crystallises in slender white needles, which are anhydrous, and insoluble in alcohol and ether. More dilute solutions yield, after some time, well defined crystals, apparently rhombohedrons containing two mols. water, which are very efflorescent, and convertible by recrystallisation into the anhydrous needles.

The barium salt, $[C_6H_3Br(NH_2)SO_3]_2Ba + 2H_2O$, prepared by neutralisation, is very soluble in water and in alcohol; the aqueous solution, when highly concentrated, solidifies to a radio-crystalline mass. The lead salt $[C_6H_3Br(NH_2)SO_3]_2Pb$, separates from a very concentrated solution as a brown, indistinctly crystalline mass, which redissolves very easily in water. Silver salt, $C_6H_3Br(NH_2)SO_3Ag$.

A solution of the acid neutralised with silver carbonate quickly turns red, and deposits the silver salt in nodular groups of brown needles.

To determine the position which the NO_2 group takes up relatively to the NH_2 on entering into orthobromobenzenesulphonic acid, the following experiments were made:—(1.) The amidobromobenzenesulphonic acid was debrominated by heating with hydriodic acid and phosphorus. (2.) The same amido-acid was converted by the diazo-reaction into dibromobenzenesulphonic acid.

(1.) *Metamidobenzenesulphonic acid*, $C_6H_4(NH_2).SO_3H$, obtained in the manner just stated, crystallised in slender needles. Its barium salt, treated with excess of bromine, did not give any precipitate of tribromaniline and sulphate of barium. Its lead salt, $[C_6H_4(NH_2)SO_3]_2Pb$, crystallised in large, six-sided, brownish, anhydrous prisms, somewhat sparingly soluble in cold water.

The *diazo-compound* of amidobromobenzenesulphonic acid is formed by the action of nitrous acid, and consists of small needles, which explode when heated or struck. They are converted by hydrobromic acid into *paradibromobenzenesulphonic acid*, $SO_3H : Br : Br = 1 : 2 : 5$. The potassium salt of this acid crystallises in white, easily soluble needles; the barium salt in white plates, not easily soluble.

Paradibromobenzenesulphochloride forms well-shaped crystals, melting at 71°. *Paradibromobenzenesulphamide* consists of long white needles, which melt at 192°.

The above reactions show that when NO_2 enters into orthobromobenzenesulphonic acid it takes the para-position.

The second *nitrobromobenzenesulphonic acid* mentioned above as being formed by the action of nitric acid on orthobromobenzenesulphonic acid, occurs only in small quantities. Its potassium salt is anhydrous, and consists of small nacreous plates, easily soluble in water. The barium salt is also anhydrous, and forms similar crystals.

Nitrobromobenzenesulphochloride, crystallises from ether in transparent prisms and rhombic plates. It melts at 97°. *Nitrobromobenzenesulphamide* consists of microscopic needles, which melt at 215°.

Amidobromobenzenesulphonic acid, formed by the action of tin and hydrochloric acid, consists of well shaped, yellowish, pointed prisms, easily soluble in hot water. When heated they carbonise without melting. The barium salt of this acid forms small warty masses. The quantity of the nitrobromobenzenesulphonic acid was too small to settle the question of its structure.

Orthochlorobenzenesulphonic acid.—The diazo-compound of ortho-amidobenzenesulphonic acid was decomposed by hydrochloric acid (saturated at 0°), under a pressure of 300 m.m. of mercury. After evaporation to dryness, the barium salt, and from this the potassium salt was prepared. The latter, when treated with phosphorus chloride, yielded orthochlorobenzenesulphochloride, which could not, however, be crystallised. The chloride was then converted into the amide, and this was heated with hydrochloric acid in a sealed tube to 180°, and the potassium salt and chloride again prepared.

Orthochlorobenzenesulphochloride crystallises from ether in colourless, solid prisms, melting at 28·5°.

Orthochlorobenzenesulphamide melts at 188°.

The statement of Limpricht (*Annalen*, clxxx, 110) must, therefore, be corrected.

Orthiodobenzenesulphonic acid is formed when fuming hydriodic acid reacts on the diazo-compound of orthoamidobenzenesulphonic acid. The barium salt is anhydrous, and consists of small white needles, easily soluble in hot water. The potassium salt contains one molecule of water, and crystallises in transparent, well formed, apparently clinorhombic crystals, which are tolerably soluble.

Iodobenzenesulphochloride is prepared by acting on the potassium salt with phosphorus pentachloride. It crystallises in solid transparent prisms, which melt at 51°.

Iodobenzenesulphamide consists of small white plates, soluble with difficulty in water. It melts at 170°.

The melting-points of the chlorides and amides of the ortho-, nitro-, chloro-, bromo-, and iodobenzenesulphonic acids are shown in the following table:—

	Chloride.	Amide.
Orthonitrobenzenesulphonic acid	67°	188°
Orthochlorobenzenesulphonic acid	28·5	188
Orthobromobenzenesulphonic acid	51	186
Orthoiodobenzenesulphonic acid	51	170

G. T. A.

Preparation of Isomeric Xylenesulphonic Acids. By F. WITTING and JULIEN POST (*Deut. Chem. Ges. Ber.*, x, 745).—Equal volumes of Kahlbaum's so-called pure xylene, boiling at 139—141°, and of pure fuming sulphuric acid were mixed together, and the liquid diluted and treated with barium carbonate; no good separation of the barium salts could be effected by crystallisation, but on conversion into potassium salts, treatment with phosphorus pentachloride, and decomposition of the oily chlorides with ammonia, two amides were obtained, easily separable by fractional crystallisation from water: after purification by recrystallisation from alcohol and ether, these melted at 123° and 130° respectively. Heating with hydrochloric acid to 150—180°, regenerated only minute quantities of the sulphonic acids, and at upwards of 180° only xylene and sulphuric acid were obtained.

C. R. A W.

Preparation of Toluenedisulphonic Acid. By R. GNEHM and K. FORRER (*Deut. Chem. Ges. Ber.*, x, 542—544).—The authors obtain toluenedisulphonic acid by the following process:—Sulphuric anhydride (3 or 4 parts) is melted in a capacious flask by means of hot water; 1 part of toluene is added thereto in small portions, and the mixture is heated to 150—180° for two hours, and ultimately to about 200° for a short time. The dark syrupy liquid thus formed contains a disulphonic acid, which appears to be identical with Blomstrand's α-toluenedisulphonic acid.

The *barium salt*, $C_6H_3(CH_3)SO_3)_2Ba + H_2O$, obtained by neutralising the acid with barium carbonate, is very freely soluble in water, and crystallises with difficulty. The water of crystallisation is expelled only above 100°.

The *potassium salt*, $C_6H_3(CH_3)(SO_3K)_2 + H_2O$, is deposited from aqueous solution in crystalline crusts. It is less freely soluble than the barium salt.

The *ammonium salt* crystallises in colourless, transparent prisms.

Toluenedisulphonic chloride is readily formed by the action of phosphorus pentachloride on the potassium salt. It crystallises from ether in prisms, which melt at 52°. When heated with alcoholic ammonia it yields the *amide*, which crystallises from alcohol or water in prisms melting at 185—186°. J. R.

Dinitrotoluenesulphonic Acids. By HUGO SCHWANERT (*Liebig's Annalen*, clxxxvii, 342—370).—Two dinitrotoluenesulphonic acids can be obtained either from a mixture of toluene and fuming sulphuric acid, which gives rise to *para-* and *ortho*toluenesulphonic acids, or from a mixture of toluene and fuming sulphuric and concentrated nitric acids, which produce orthonitroparatoluenesulphonic acid and paranitroorthotoluenesulphonic acid, the nitration being in either case completed by long continued boiling with concentrated nitric acid. One of these, viz., *dinitroparatoluenesulphonic acid*, is formed in much the larger quantity; the other, *dinitroorthotoluenesulphonic acid*, yields a barium salt, much more soluble than that of the other acid, so that the dinitroparasulphonic acid is readily obtained pure. The author describes the mode of preparation of this acid from pure toluenepara-sulphonic acid, and from pure orthonitroparatoluenesulphonic acid, as well as those of the corresponding dinitroorthosulphonic acid; also the potassium, ammonium, barium, lead, and copper salts of the dinitroparasulphonic acid and its chloride (melting point, 125°) and amide (melting point, 203°). By reduction with ammonium sulphhydrate, *diamidoparatoluenesulphonic acid* is formed, soluble in 1470 parts of water, at 14°, and not fusible at 280°; the barium, lead, and potassium salts of this acid were prepared, and also the compounds of this acid with hydrochloric acid, $C_6H_2(CH_3)(NH_2)_2(SO_3H).HCl.2H_2O$; with hydrobromic acid, $C_6H_2(CH_3)(NH_2)_2(SO_3H)$, HBr, $2H_2O$; with sulphuric acid $\{C_6H_2(CH_3)(NH_2)_2(SO_3H)\}_2$, H_2SO_4, H_2O; and with nitric acid, $C_6H_2(CH_3)(NH_2)_2(SO_3H).HNO_3.H_2O$; in all of which the diamido-acid acts as a mono-acid base. By bromination, *bromodiamidoparatoluenesulphonic acid*, $C_6H.Br(CH_3)(NH_2)_2(SO_3H)$, is formed; further bromination gives rise to *dibromdiamidoparatoluenesulphonic acid*, but a considerable quantity of bye-products are also formed through other changes. Nitrous acid gives rise to a dark brown-red amorphous diazoderivative. C. R. A. W.

Aromatic Sulphones. By A. MICHAEL and A. ADAIR (*Deut. Chem. Ges. Ber.*, x, 583—587).—The authors have discovered a general reaction by which this class of bodies may be prepared. It consists in the action of phosphoric anhydride, at high temperatures, on a mixture of an aromatic sulphonic acid with a hydrocarbon. They have hitherto experimented with mixtures of benzenesulphonic acid and toluene, benzenesulphonic acid and naphthalene, paratoluenesulphonic acid and benzene, and β-naphthalenesulphonic acid and benzene, all of which yield sulphones when heated with phosphoric anhydride. The following two products of the reaction have been more fully investigated.

α- and β-Naphthylphenylsulphones.—These bodies are formed simultaneously when a mixture of equal weights of benzenesulphonic acid and naphthalene is heated to 170—190° with phosphoric anhydride in a sealed tube for some hours. They are separated by crystallisation from ether-alcohol, in which the β-compound is the more soluble.

The α-compound crystallises in fine rhombohedral crystals, melting at 99·5—100·5°. It dissolves sparingly in cold alcohol and ether, but very freely in the hot liquid; and is very soluble also in hot benzene and glacial acetic acid, but insoluble in water.

The β-compound crystallises from alcohol in long needles, which melt at 115—116°. In point of solubility it resembles the α-compound. It possesses a lustre like that of naphthalene, whereas the α-compound is lustreless.

A mixture of β-naphthalenesulphonic acid and benzene, when heated with phosphoric anhydride, yields a substance apparently identical with β-naphthylphenylsulphone. J. R.

Decomposition of Phenol at a Red Heat. By J. G. KRAMERS (*Arch. Pharm.* [3], x, 440—445).—The phenol was passed through a red-hot iron tube. Benzene, toluene, naphthalene, anthracene, and a substance isomeric with fluorene ($C_{13}H_{10}$) were obtained. From 4 litres of phenol about 1 litre of liquid decomposition-products was obtained; of this about 400 c.c. consisted of benzene. When phenol was passed through a red-hot glass tube, a small quantity of benzene was also obtained. M. M. P. M.

Resorcin. By L. CALDERON (*Compt. rend.*, lxxxiv, 1164—1166). —From his determinations of the molecular volumes of resorcin in aqueous solutions at different temperatures, the author concludes that the substance exists in the solutions as if in the solid state and isolated from the solvent. Resorcin, in presence of water and potash, very slowly absorbs oxygen. In a sealed tube it may be subjected to a temperature of 120° for an indefinite time, without undergoing any change. If, however, it be heated to this temperature with access of air, a portion is volatilised, whilst another portion is converted into a reddish substance, which appears to be a product of oxidation.

R. R.

Action of Fuming Sulphuric Acid on Resorcin. By J. ANNAHEIM (*Deut. Chem. Ges. Ber.*, x, 975).—By acting on two molecules of phenol with one of fuming sulphuric acid, oxysulphobenzide is produced. Cresol under similar treatment forms a body soluble in acetic acid with a fuchsine red colour. Resorcin, when heated to 120—130° for an hour or two with the same proportion of acid, forms a substance but little soluble in water, but soluble in alcohol, glacial acetic acid, and alkalis with a red colour, the latter solutions (especially the ammoniacal one) showing a fine fluorescence. Water precipitates the body from the alcoholic solution; acids from the alkaline liquors. Bromine and iodine form fluorescent bodies by their action on this substance.

C. R. A. W.

Styrolene Alcohol or Phenylglycol. By C. WACHENDORFF and TH. ZINCKE (*Deut. Chem. Ges. Ber.*, x, 1004—1007).—This glycol was prepared from styrolene dibromide, which was converted into the acetate or benzoate, and these ethers were saponified by potash. Styrolene alcohol, $C_6H_5.CH(OH).CH_2.OH$, is readily soluble in water, alcohol, ether, benzene, and acetic acid, sparingly in petroleum naphtha, and is best crystallised from a mixture of the latter with benzene. It forms thin, silky needles, melting at 67—68°. The diacetate was obtained pure by the action of acetyl chloride or anhydride on the alcohol, and is an oily liquid, having a faint aromatic smell. The dibenzoate crystallises in small, white needles, which melt at 96—97°, and can be sublimed. On boiling the alcohol with dilute sulphuric acid, a liquid having a penetrating smell is formed, consisting probably of the corresponding pinacolin, which is probably phenylacetic aldehyde, $C_6H_5.CH_2.COH$.

C. S.

Quinones. By E. CARSTANJEN (*J. pr. Chem.* [2], xv, 398—417).—Oxythymoquinone may be obtained by careful sublimation of *large* quantities in two isomeric modifications, one of which consists of light, orange-coloured, acicular crystals, melting between 169° and 175°, the other of dark red crystals, which melt between 183° and 221°. The oxythymoquinone used by the author was prepared by reduction of dinitrothymol (from thymol) and oxidation of the diamido-compound. Thymol is a definite body, and the dinitro-compound also, *i.e.*, it is not a mixture of isomeric compounds, so that, according to the present view of the constitution of the quinones, only one oxythymoquinone should be possible. In order to account for the two isomeric oxythymoquinones, the author supposes that several different hydrogen pairs exist in benzene, which can be replaced by the group O_2, and that therefore benzene is capable of yielding two isomeric quinones, according as the oxygen atoms assume the ortho- or the para-position. Several experiments are described, which bear out this view.

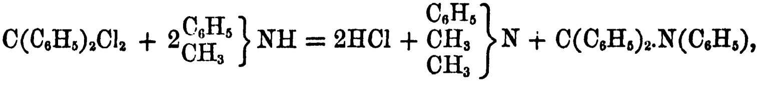
G. T. A.

Ammonia Derivatives of Benzophenone and Acetone. By M. PAULY (*Liebig's Annalen*, clxxxvii, 198—216).—When 1 molecule of benzophenone chloride, $C(C_6H_5)_2Cl_2$, is made to act on 4 mols. aniline, the mixture being carefully cooled, a vigorous reaction takes place and the whole becomes crystalline, *diphenylmethylene-aniline* being formed in virtue of the reaction—

$$C(C_6H_5)_2Cl_2 + NH_2C_6H_5 = 2HCl + C(C_6H_5)_2{=}N(C_6H_5).$$

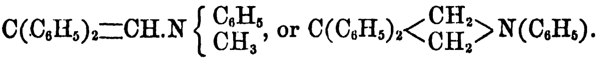
By treatment of the product with water and ether, and recrystallisation from hot absolute alcohol of the residue left on evaporating the ether, the new body is obtained in rhombic crystals melting at 109° (not corrected), and volatile without decomposition at a temperature above the boiling point of mercury. The "ditoluidine-diphenamine" of Schiff, obtained by the action of bitter almond oil on aniline, is apparently closely related to this body, being $CH(C_6H_5){=}N(C_6H_5)$; Laurent and Gerhardt term it "benzoylanilide." Acids dissolve diphenylmethylene-aniline, decomposing it into aniline and benzophenone; the same result is produced when platinic chloride is added to its alcoholic solution; heating with water to 180—200° for ten hours, however, produces no change.

If methylaniline be employed instead of aniline, the following reaction ensues:—



$$C(C_6H_5)_2Cl_2 + 2\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}NH = 2HCl + \left.\begin{matrix}C_6H_5\\CH_3\\CH_3\end{matrix}\right\}N + C(C_6H_5)_2.N(C_6H_5),$$

i.e., dimethylaniline and diphenylmethylene-aniline are formed. Ethylaniline behaves similarly, but dimethylamine forms a base, $C_{21}H_{19}N$, this being either—



$$C(C_6H_5)_2{=}CH.N\left\{\begin{matrix}C_6H_5\\CH_3\end{matrix}\right., \text{ or } C(C_6H_5)_2<\begin{matrix}CH_2\\CH_2\end{matrix}>N(C_6H_5).$$

This substance forms salts with acids, its platinum salt being $(C_{21}H_{19}N, HCl)_2PtCl_4$; at the same time a small quantity of a base, apparently $C_{17}H_{24}N_2$, is formed.

In the same way, toluidine and benzophenone chloride yield *diphenylmethylene-toluidine*, $C(C_6H_5)_2{=}N(C_6H_4.CH_3)$, a highly refractive liquid, decomposed by acids into benzophenone and toluidine naphthylamine, and benzophenone chloride gives rise to *diphenylmethylene-naphthylamine*, $C(C_6H_5)_2{=}N(C_{10}H_7)$, crystallising in golden rhombic plates and decomposed by acids into benzophenone and naphthylamine. Ammonia in ethereal solution has no action whatever on benzophenone chloride, even in sealed tubes at 130°; alcoholic ammonia, however, forms benzophenone and ethylamine, thus—

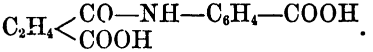
$$C(C_6H_5)_2Cl_2 + C_2H_5OH + NH_3 = C(C_2H_5)_2O + 2HCl + C_2H_5.NH_2.$$

On benzophenone itself ammonia has no action, even at 200°, in absolute alcohol solution.

According to Schiff, acetone and aniline do not react on one another; Engler and Heine found that under the influence of water-abstracting substances a little of a base, apparently $C(CH_3)_2{=}N(C_6H_5)$, is formed. On heating a salt of aniline (hydrochloride) with acetone for three days to 180° in sealed tubes, there are formed inflammable gases and bases boiling at 230—235° and higher: that passing near 230° appears to be Engler and Heine's base in an impure state. C. R. A. W.

Preparation of Paramidobenzoic Acid. By A. MICHAEL (*Deut. Chem. Ges. Ber.*, x, 576—580).—This body cannot be obtained by the direct oxidation of toluidine, the product thus obtained being, as is well known, azotoluene. But the author has found that, on replacing hydrogen-atoms in the amido-group of toluidine by acid radicles, the bodies thereby formed are capable of yielding by oxidation derivatives of paramidobenzoic acid, and from these the acid itself may be obtained by further treatment. He has operated upon the succinyl- and phthalyl-derivatives of toluidine (paratolylsuccinimide and paratolylphthalimide).

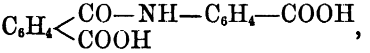
Paratolylsuccinimide (obtained by distilling a mixture of solid toluidine and succinic acid) in very dilute hot aqueous solution, yields by oxidation with potassium permanganate (4 or 6 mols.), an acid called by the author *oxysuccinylparamidobenzoic acid.* This substance crystallises in yellow needles, which melt at 225—226°. It dissolves very sparingly in water, but easily in alcohol, and also in ammonia, with which it forms a freely soluble ammonium-salt. From this last, barium, lead, copper, and silver salts have been obtained by precipitation. The constitution of the acid is represented by the formula—



$$C_2H_4{<}\begin{matrix}CO{-}NH{-}C_6H_4{-}COOH\\COOH\end{matrix}.$$

Oxysuccinylparamidobenzoic acid, when boiled with hydrochloric acid, yields the hydrochloride of paramidobenzoic acid, which when treated with sodium carbonate and then acidified, gives paramidobenzoic acid. The yield is very satisfactory.

Paratolylphthalimide was obtained by distilling together equal numbers of molecules of solid toluidine and phthalic acid. It is insoluble in water, but soluble in hot alcohol, from which it crystallises in needles melting at 200°. When cautiously heated it sublimes in long needles. Like the succinyl-compound it is oxidised by potassium permanganate, and thus yields *oxyphthalyl-paramidobenzoic acid*—



$$C_6H_4{<}\begin{matrix}CO{-}NH{-}C_6H_4{-}COOH\\COOH\end{matrix},$$

a body melting at 275—277°, and giving paramidobenzoic acid by the treatment described above. J. R.

Properties of the Acid $C_9H_6O_3$ from Benzoyl Cyanide. By L. CLAISEN (*Deut. Chem. Ges. Ber.*, x, 844—848).

—The phenylglyoxylic acid, $C_6H_5.CO.CO_2H$, which is obtained by the action of cold hydrochloric acid on benzoyl cyanide, is different from the phenyloxylic acid which Hübner and Buchka prepared by heating the cyanide with the dry gaseous acid. Its ethylic ether is a yellowish-green aromatic oil boiling at 250—255°. Alcoholic potash saponifies it at once, with formation of $C_8H_5O_3K$, which is almost insoluble in cold alcohol, and crystallises from hot alcohol in flat prisms. $C_8H_5O_3Ag$ is a crystalline precipitate separating from a hot aqueous solution in small four- or six-sided plates. On decomposing the salts with an acid, phenylglyoxylic acid separates as an oil, solidifying in an exsiccator to a crystalline mass melting at 65—66°. Sodium-amalgam and water convert it into mandelic acid, and on heating it with strong hydriodic acid and phosphorus, it yields α-toluic (phenylacetic) acid.

C. S.

Abnormal Solubility of Zinc Xylidate. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, x, 857—860).—By shaking pseudocumene with a warm solution of potassium permanganate it is oxidised to xylidic acid, which can be easily recognised by its zinc-salt. 100 parts of water dissolve at 0° 36 parts, at 100° only 0·735, or at 130° nearly 0·5. The graphic curve shows that no maximum of solubility exists; from a solution saturated at −4° the anhydrous salt crystallises at +4°; a hydrated salt cannot be obtained. C. S.

Nitrosalicylic Acid. By T. L. PHIPSON (*Compt rend.*, lxxxiv, 1034).—Salicylic acid suspended in water, to which nitric acid is added, dissolves with production of a deep red colour when the liquid is heated. A strong odour of the plant *Spiræa ulmaria* is given off during the solution, and the author has found that a considerable quantity of salicylic aldehyde is, in fact, formed under these circumstances. This can be separated from the brown liquid from which the nitrosalicylic acid has crystallised out, by agitation with ether. The evaporation of the ethereal solution leaves the nitrosalicylic aldehyde as a reddish, strongly odorous oil. R. R.

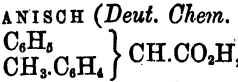
Benzyl- and Dibenzyl-acetic Acids. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 758).—By acting on acetic ether with sodium and on the product with benzyl chloride, an oily liquid is obtained from which by fractional distillation two portions are separable boiling at 245—250° and upwards of 300° respectively. On saponification, these form *benzyl-acetic acid* (phenyl-propionic acid or hydrocinnamic acid) and *dibenzyl-acetic acid* respectively. The first melts at 47° and is identical with Erlenmeyer's hydrocinnamic acid; the second melts at 85°, and forms anhydrous silver and barium salts, the calcium salt being $(C_{16}H_{15}O_2)_2Ca,H_2O$; with salts of the heavy metals its ammonium salt forms precipitates often of characteristic colours. On distilling the acid or its barium salt with soda-lime *dibenzyl-methane*, $CH_2(C_7H_7)_2$, is formed; this forms a crystallisable bromo-substitution-product and a dinitro derivative. C. R. A. W.

Metanitro- and Metamidobenzacetic Acid. By L. LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 861—866).—By adding silver metanitrobenzoate to an excess of acetyl chloride, an acid, $C_9H_7NO_5$, is obtained which crystallises in pointed prisms, melting at 130—132°. It dissolves freely in hot water, alcohol, and ether, and more sparingly in cold water; on heating it explodes. Only the lead salt, $(C_9H_6NO_5)_2Pb + 2H_2O$, could be obtained pure by shaking a cold solution of the acid with lead oxide; it forms thin prisms. Sulphide of ammonium reduces the acid to an isomeride of hippuric acid, $C_9H_9NO_3$, which is readily soluble in water.

As the nitro-acid has a strong acid reaction, and is not decomposed by recrystallisation, nor yields acetic acid on distillation with water or dilute acids, the author believes it to have the constitution—

$$C_6H_4\left\{\begin{array}{l}CO.CH_2.CO.OH\\NO_2\end{array}\right. .$$

C. S.

Paratolylphenylacetic Acid. By H. TANISCH (*Deut. Chem. Ges. Ber.*, x, 996—999).—*Tolylphenylacetic acid*,  $\left.\begin{matrix}C_6H_5\\CH_3.C_6H_4\end{matrix}\right\}CH.CO_2H$, is easily obtained by heating phenylbromacetic acid with toluene and zinc dust. The product is a mixture of the para- and the ortho-compound, the former predominating. Paratolylphenylacetic acid is sparingly soluble in cold water, a little more freely in boiling water, and readily in alcohol, ether, chloroform, and carbon sulphide. It crystallises in nearly rectangular plates, melting at 115°, and subliming, when more strongly heated, in oily drops, which gradually solidify and then melt at 108—110°.

The potassium salt crystallises from a concentrated solution in clear, monoclinic plates, containing 4 mol. of water. The sodium salt is very soluble, and forms needles with 6 mol. of water. The barium salt could be obtained only as a resinous mass, and the calcium salt, which is well adapted for the purification of the acid, is very sparingly soluble in cold and hot water, and crystallises from dilute hot alcohol in glistening needles, containing 2 mols. of water. The salts of lead, copper, silver, and zinc are precipitates; the first crystallises from hot alcohol in needles; the copper and zinc salts dissolve also in alcohol, and more freely in ether alcohol, separating in viscid drops, which gradually solidify. The methyl-ether is a thick oil, and the ethyl-ether crystallises from alcohol in plates melting at 34°. The amide forms needles, which are grouped in warty masses, and melt at 151°. The soluble salts of the acid are decomposed by carbon dioxide. Chromic acid solution oxidises the acid to paratolylphenyl ketone and parabenzoylbenzoic acid.

On purifying the crude acid by crystallisation from alcohol, a mother-liquor is obtained, containing an oily acid, which could not be crystallised, and consists of a mixture of the para- and ortho-acids. A separation of these could not be effected, but their presence was proved by oxidation, a mixture of para- and ortho-benzoylbenzoic acid being formed. C. S.

Rufigallic Acid. By W. KLOBUKOWSKY (*Deut. Chem. Ges. Ber.*, x, 880—888).—The number of acetyl-groups in acetylrufigallic acid cannot be ascertained by combustion-analysis, as the replacement of hydrogen by acetyl makes but little difference in the percentage composition. They can, however, be determined by decomposing with an alkali and weighing the rufigallic acid. But as the blue alkaline solution of the latter rapidly absorbs oxygen with formation of black products, all operations must be performed in an atmosphere of hydrogen. Two experiments gave 54·25 and 54·12 per cent., while the formula $C_{14}H_2(C_2H_3O)_6O_8$ requires 54·68. Schiff, who obtained an acetyl-compound by heating the acid with acetic anhydride, analysed it by decomposing it with magnesia, and obtained numbers agreeing with the formula $C_{14}H_4(C_2H_3O)_4O_8$. But on preparing the compound by Schiff's method and analysing it as above, found 54·34 per cent. of rufigallic acid.

When rufigallic acid is heated with an excess of monochloracetyl chloride, only one hydroxyl is replaced, the compound $C_{14}H_7(C_2H_2ClO)O_8$

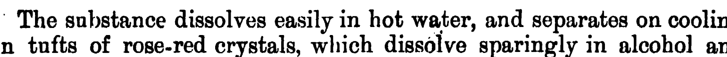
being formed, crystallising from acetic acid in microscopic yellowish-brown needles.

On heating rufigallic acid with an excess of methyl iodide, potash, and dilute methyl alcohol for 3—4 hours to 120—130°, it forms *tetramethyl rufigallic acid*, $C_{14}H_4(CH_3)_4O_8$, crystallising from acetic ether in red plates or needles, with a brilliant golden lustre. It dissolves in boiling concentrated potash slowly, with a red colour, and melts at about 220°. On dissolving it in concentrated sulphuric acid, a deep-red liquid is obtained, from which water precipitates yellow flakes.

Tetrethylrufigallic acid, $C_{14}H_4(C_2H_5)_4O_8$, is formed under similar conditions, and crystallises from alcohol in ruby-red needles, melting a little above 180°. It is freely soluble in chloroform, carbon sulphide, benzene, acetic ether and hot acetic acid, more sparingly in alcohol and less in ether. In boiling alkalis, it dissolves slowly with a red colour, and its red solution in sulphuric acid gives with water a white precipitate. On heating it again with potash and ethyl iodide, the hexethyl compound, $C_{14}H_2(C_2H_5)_6O_8$, is formed, which readily dissolves in ether, carbon sulphide, benzene, and hot acetic acid, with a yellow colour, and crystallises from hot dilute alcohol in orange-coloured needles, melting a little above 140°. It is not soluble in alkalis; sulphuric acid yields with it a deep-red solution, which is precipitated yellow by water. From these experiments, it follows that rufigallic is really a hexhydroxyl-anthraquinone.

On heating protocatechuic acid with sulphuric acid, only a small quantity of a blackish-brown compound was obtained, and by using a mixture of gallic and salicylic acid, a product having the properties of rufigallic acid was formed. C. S.

Diamidosulphobenzide - Dicarbonic Acid. By ARTHUR MICHAEL and H. NORTON (*Deut. Chem. Ges. Ber.*, x, 580—583).—A substance thus named by the authors is obtained by the action of fuming sulphuric acid on paramidobenzoic acid at 170—190°. Its composition agrees with the formula $C_{14}H_{12}N_2SO_6$. Its formation may be represented by the equation—



$$2C_6H_4(NH_2)COOH + H_2SO_4 = 2H_2O + SO_2 < \begin{matrix} C_6H_3(NH_2)COOH \\ C_6H_3(NH_2)COOH \end{matrix}.$$

The substance dissolves easily in hot water, and separates on cooling in tufts of rose-red crystals, which dissolve sparingly in alcohol and ether, and very slightly in chloroform. It dissolves readily in alkalis, forming neutral, easily soluble salts.

The *ammonium salt* crystallises in fine laminæ; the *potassium salt* in small needles.

The *barium salt* is very freely soluble in water.

The *lead salt*, obtained by precipitation, is white, and nearly insoluble in water.

The silver salt, $C_{14}H_{10}Ag_2N_2SO_6$, is precipitated in small white laminæ, on adding silver nitrate to the ammonium salt. It is insoluble in cold water, and gradually turns brown in the light.

J. R.

On a new Naturally-occurring Organic Acid. By C. STAHLSCHMIDT (*Liebig's Annalen*, clxxxvii, 177—197).—This acid occurs in the free state in a fungus which grows on diseased or decaying oaks. The author has not been able to discover the exact species to which the fungus belongs, but it seems to be closely allied to *Polyporus purpurascens*. It may be recognised by the following characteristics:—(1). It grows (perhaps only) on decaying oaks; is semicircular in shape, and rests directly on the bark without any stalk, somewhat like half a saucer with the thick part towards the bark. It is easily detached. (2). The colour of the dry fungus is exactly that of yellow German tinder, or yellow ochre. In wet weather it becomes brownish-yellow. (3). When brought into contact with dilute ammonia, its colour changes to a fine deep violet, and it yields a solution from which hydrochloric acid throws down a yellow precipitate of the new acid—polyporic acid.

To prepare the acid, the fungus is washed with water and then steeped in dilute ammonia for twenty-four hours. By this means the acid is converted into its ammonium-salt, which is soluble in water, though the acid itself is totally insoluble. The ammonium polyporate is next decomposed by hydrochloric acid, and the precipitated acid, after filtering and washing, is treated with caustic potash, and thus converted into potassium polyporate, which is washed for some time with caustic potash, in which it is insoluble. It is then washed with alcohol till free, as far as possible, from potash, and dissolved in hot water. Carbon dioxide is passed into the liquid to convert any remaining traces of potash into the carbonate, and it is then crystallised several times. The polyporic acid is finally precipitated by hydrochloric acid.

Properties of Polyporic Acid.—Its colour is that of the fungus, and it is totally insoluble in water; so that the slightest trace of a soluble polyporate shows a turbidity on addition of an acid. The soluble polyporates might, therefore, be used as indicators in alkalimetry. The acid is also insoluble in ether, benzene, bisulphide of carbon, and acetic acid. It dissolves very slightly in chloroform, amyl alcohol, and boiling (95 per cent.) alcohol. From the latter solvent it crystallises in small rhombic plates, which exhibit a lively bronze colour when dry. It contains no water of crystallisation, and becomes strongly electrical when rubbed in the dry state. It may be heated without change to 220°; but at a higher temperature it melts, and sublimes, with partial decomposition, evolving a smell of heated or burning oak-branches, and after a time that of bitter almond oil. The formula of dry polyporic acid is $C_9H_7O_2$.

Salts of Polyporic Acid.—Polyporic acid forms salts with all the bases. The easily soluble salts—those of the alkali-metals and ammonia—form violet solutions, which cannot be distinguished in appearance from a concentrated solution of potassium permanganate. All the salts are decomposed by the stronger acids, even by acetic acid, at ordinary temperatures, with perfect separation of the polyporic acid; but when polyporic acid is boiled with potassium or sodium acetate, the acetic acid is expelled, and a polyporate is formed. All the polyporates, except that of ammonium, can be heated to over 200°, without decomposition.

Potassium polyporate, $C_9H_6O_2K + H_2O$, crystallises in the form of gypsum. It does not lose its water of crystallisation when dried over sulphuric acid, but loses it completely when heated to 120°.

Sodium polyporate, $C_9H_6O_2Na + H_2O$, obtained by neutralising the acid with dilute caustic soda, is insoluble in concentrated caustic soda, and loses its water of crystallisation at 180°.

Ammonium polyporate, $C_9H_6O_2NH_4 + H_2O$, loses not only its water of crystallisation, but also the whole of its ammonia, by long standing in the air, or by heating to 100°.

Barium polyporate, $(C_9H_6O_2)_2Ba + 4H_2O$, loses 2 molecules of water at 120°, and the other 2 at 150 to 160°.

If the salt containing 4 molecules of water is boiled for a time, another salt is precipitated, which has the composition $(C_9H_6O_2)_2Ba + 2H_2O$. This is also quite insoluble in water, possesses a metallic lustre, and loses its water of crystallisation at 180°.

Strontium polyporate, $(C_9H_6O_2)_2Sr + 4H_2O$, is insoluble in water. It is not altered by boiling, but is converted by a heat of 120° into a salt of the composition $(C_9H_6O_2)_2Sr + H_2O$. It loses the last molecule of water at 180—200°.

Calcium polyporate, $(C_9H_6O_2)_2Ca + 3H_2O$, is slightly soluble in water. At 120° it loses 2 molecules of water, and leaves a salt of the composition $(C_9H_6O_2)_2Ca + H_2O$. At 180° it becomes anhydrous.

Magnesium polyporate, $(C_9H_6O_2)_2Mg + 3H_2O$, is so sparingly soluble, that ammonium polyporate can be used for the separation of magnesia from the alkalis.

Silver polyporate, $C_9H_6O_2Ag$, is quite insoluble in water, and cannot be distinguished in appearance from the acid itself. It is anhydrous, and undergoes no change by boiling with water or heating to 150°.

The combinations of the acid with the rest of the metals consist of insoluble amorphous precipitates.

The methyl ether, $C_9H_6O_2.CH_3$, is obtained by the action of silver polyporate on methyl iodide. It may be crystallised from boiling alcohol (95 per cent.). This ether melts at 187°; it is decomposed by heating with potash or ammonia, the corresponding polyporate being regenerated.

The *ethyl ether* may be formed in the same way as the foregoing. It melts at 134°.

Acetopolyporic acid, $C_9H_6O_2.C_2H_3O$, is formed when polyporic acid is heated to 150—170° in closed tubes, with excess of acetic anhydride. It melts at about 205°.

Polyporic acid is violently acted on by concentrated nitric acid, but the products of the reaction have not yet been fully investigated.

When polyporic acid is added to a cold mixture of potassium chlorate and hydrochloric acid, it is converted into a bright-yellow compound, soluble in alcohol; but if the acid is added to boiling hydrochloric acid, and potassium chlorate is introduced little by little, an oily body gradually forms at the bottom of the vessel, becoming solid on cooling. This body is partly soluble in boiling water, and the solution deposits snow-white feathery crystals, which are easily soluble in caustic potash, and appear to consist of an acid containing chlorine (34·5 per cent.). The part which is insoluble in water dissolves easily in alcohol, and separates in long, golden, slender needles. This body possesses very great capabilities of crystallisation. Heated with caustic potash, it evolves a smell of bitter almonds, and forms a dark-red substance, which is totally insoluble in alcohol, ether, alkalis, &c. The yellow compound (containing 38·7 per cent. of chlorine) is decomposed on heating, and emits a smell of benzoyl chloride. A third body is found in the alcoholic mother-liquor of the original solution, which remains behind on evaporation of the alcohol as a thick oil. It has not been fully examined.

When potassium polyporate is boiled for some time with excess of concentrated caustic potash, the violet colour of the solution gives way to a yellowish-red one, and the smell of bitter almonds becomes perceptible. On cooling, fine colourless needles are deposited. The alkaline solution becomes turbid on addition of hydrochloric acid, and on standing a dull-yellow body separates, which is soluble in alcohol, and forms compounds with alkalis.

Addition of zinc-dust to an alkaline solution of potassium polyporate renders the solution colourless, but it becomes red again on exposure to air. When amomnium polyporate, mixed with excess of ammonia, is left to stand, a decomposition or alteration of the acid takes place, and the liquid becomes blue and fluorescent. At a higher temperature the change takes place more quickly, and a brown insoluble body is formed.

Benzene was obtained by heating potassium polyporate to a high temperature with zinc-dust, which, with the behaviour of the acid to concentrated caustic potash, would show that polyporic acid belongs to the aromatic series.

The author will shortly publish further investigation on the character of the acid, and the products of decomposition mentioned above. G. T. A.

Compounds of the Hydrobenzoïn-group. By TH. ZINCKE (*Deut. Chem. Ges. Ber.*, x, 999—1004).—By the action of phosphorus pentachloride on hydrobenzoïn, two chlorides, $C_{14}H_{12}Cl_2$, are formed, one melting at 191—192°, and the second at 93—94°. Isohydrobenzoïn yields only the high-melting chloride and a considerable quantity of a resinous body containing chlorine. The first chloride is sparingly soluble in hot alcohol, from which it crystallises in slender needles. Larger prismatic crystals are obtained from a solution in toluene, and by the slow evaporation of its solution in ether or chloroform well-defined crystals are formed. On heating it repeatedly above 200° the melting point is lowered to 160—165°. The chloride melting at 93—94° is more readily soluble than the first, and crystallises from alcohol or petroleum-naphtha in four- or six-sided plates or prisms, possessing an aromatic odour. By heating it several times above its melting point the latter rises and becomes constant at 160—165°. It consists now, as well as that obtained by heating the higher-melting modification, of a mixture of the latter with a more soluble lower-melting chloride, which is probably identical with that having the melting point 93—94°.

Phosphorus trichloride converts both alcohols into the chloride melting at 191—192°. The acetate formed by the action of silver acetate on this, as well as on the other modification, yields by saponification, *isohydrobenzoïn*, and only a mere trace of its isomeride.

C. S.

α-Derivatives of Naphthalene. By A. Atterberg (*Deut. Chem. Ges. Ber.*, x, 547—550).—This is a continuation of a previous paper. The author finds that the β-dichloronaphthalene melting at 67—68° is converted, by boiling with nitric acid, into *dichlorophthalic acid*, which yields by sublimation fine needles of an anhydride melting at 185—186°. Hence he concludes that in this dichloronaphthalene both atoms of chlorine are contained in the same half of the naphthalene-molecule.

γ-Dichloronaphthalene, when similarly treated, yields a *nitrochlorophthalic acid*, $C_6H_2ClNO_2(COOH)_2$, the potassium salt of which explodes when heated to 200°.

J. R.

Azonaphthalene. By W. Klobukowski (*Deut. Chem. Ges. Ber.*, x, 570—576).—The author attempted to prepare this substance by the action of potash on nitronaphthalene, and by the action of oxidising agents on naphthylamine, but without success. He ultimately adopted a modification of the method devised by Doer. An intimate mixture of 30 grams of nitronaphthalene with 600 grams of zinc-dust, heated in an iron basin, yielded a sublimate of azonaphthalene amounting to about 4 per cent. of the nitronaphthalene employed. The product, after boiling with alcohol to free it from impurities, sublimed in fine lemon-yellow needles melting at 275°, and agreeing in composition with the formula $C_{20}H_{14}N_2$.

Azonaphthalene is nearly insoluble in alcohol, ether, glacial acetic acid, chloroform, benzene, toluene, petroleum-spirit, and carbon bisulphide, but dissolves in glacial acetic acid on addition of a few drops of fuming nitric acid. It dissolves also in boiling strong nitric acid and in strong sulphuric acid. It is not acted on by soda-ley or by potassium chlorate and hydrochloric acid. The same body is formed, though only in small quantity, by distilling nitronaphthalene with quick-lime. It is identical with Laurent's naphthase.

Azonaphthalene heated to 260° with excess of bromine, yields a body which crystallises from carbon bisulphide in small, yellow needles melting at 320°, and agreeing in composition with the formula, $C_{30}H_9Br_5N_2$.

J. R.

Azonaphthalene. By W. H. Doer (*Deut. Chem. Ges. Ber.*, x, 772).—Azonaphthalene dissolves in sulphuric acid with a beautiful violet-blue colour, as stated by Klobukowski, and not with a red tint, as originally described by the author. Its melting point is near 278° (not corrected).

C. R. A. W.

Occurrence of Methylanthracene in Coal-tar. By F. R. JAPP and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, x, 1049—1051).—Dumas and Laurent found in coal-tar a hydrocarbon to which the formula $C_{15}H_{12}$, that of methylanthracence, $C_{14}H_9.CH_3$, was assigned, but it has since been asserted that this hydrocarbon was merely impure anthracene. Methylanthracene has, however, been obtained from other sources by Weiler, by Fischer, and by Liebermann, and quite recently was observed by one of the authors (*ibid.*, x, 117) amongst the products of the decomposition of turpentine by heat. This fact suggested that it might probably be contained in coal-tar. Crude phenanthrene was therefore submitted to fractional oxidation with potassium dichromate and sulphuric acid to remove the greater part of the anthracene, and then crystallised from alcohol. The alcoholic mother-liquors were found to contain, besides phenanthrene, another hydrocarbon boiling above 360°, which was identified as methylanthracene. It crystallises from alcohol in plates which melt at 190°, and by oxidation yields anthraquinone-carbonic acid, $C_{15}H_8O_4$, identical in all its properties with that described by Weiler, Fischer, Liebermann, and vom Rath. C. E. G.

Note on the preceding Paper. By G. SCHULTZ (*Deut. Chem. Ges. Ber.*, x, 1051—1052).—The author points out that although the amount of methylanthracene obtained from the crude phenanthrene was but small, it is not improbable that a much larger proportion may be present in commercial anthracene. The ordinary method of estimating the value of anthracene would convert the methyl-derivative into anthraquinone-carbonic acid, which would be dissolved by the subsequent treatment with an alkaline solution, whilst in the process of manufacture it would be converted into methylanthraquinone. Methylanthraquinone may possibly yield methylalizarin, although this has not yet been detected in commercial alizarin; the purpuroxanthincarbonic acid of Schunck and Roemer may also be a derivative of this hydrocarbon. C. E. G.

Purpurin. By E. SCHUNCK and H. ROEMER (*Deut. Chem. Ges. Ber.*, xi, 550—556).—According to the authors, the properties of purpurin are as yet but imperfectly known, owing to the difficulty of obtaining it free from admixture with alizarin. They have examined purpurin, carefully purified by repeated crystallisation, first from alum-water and afterwards from weak spirit, with the following results:—

Pure purpurin, dried at 110°, gives on analysis numbers agreeing approximately with the formula $C_{14}H_8O_5$. It dissolves freely in alcohol, forming yellow solutions. It crystallises from weak spirit in long, orange-coloured needles containing 1 mol. of water, and from strong alcohol in smaller dark-red needles, which are anhydrous. The hydrated crystals give off their water at 100°, turning dark-red. Purpurin begins to sublime at 150°, and yields a sublimate of feathery or acicular crystals, but much of it is carbonised. The melting-point is 253°. The solution of purpurin in boiling water is dark-yellow, inclining to red, and deposits orange-coloured needles on cooling. The ethereal solution is dark-yellow and fluorescent, and exhibits two absorption-bands, one coincident with the line *F*, the other close to the line *E*. Solutions in boiling glacial acetic acid, carbon bisulphide, boiling benzene, are all dark-yellow, and exhibit the same absorption-bands as the ethereal solution. The solution in strong sulphuric acid is rose-red, and shows three absorption-bands, one in the yellow, the other two as mentioned above. Solutions of purpurin in potash, soda, ammonia, or sodium carbonate are bright-red, and exhibit two absorption-bands in the green. Purpurin is insoluble in boiling baryta- and lime-water, but yields therewith purple-red lakes. Its alcoholic solution gives a yellow precipitate with copper acetate and a reddish-violet precipitate with lead acetate.

Triacetyl-purpurin, $C_{14}H_5(C_2H_3O)_3O_5$, is formed by the action of acetic anhydride on purpurin at 180°. It melts at 198—200°. It is decomposed by dilute aqueous potash, even in the cold, yielding purpurin.

Bromo-purpurin.—Purpurin, when digested with a solution of bromine in carbon bisulphide, is converted into monobromo-purpurin, $C_{14}H_7BrO_5$. This substance crystallises from glacial acetic acid in dark-red needles, which melt at 276°. It closely resembles purpurin in most respects, but sublimes almost without decomposition.

Purpurin, when heated to 300° for several hours, is partially converted into quinizarin; much of it, however, is carbonised.

J. R.

Researches on Pseudopurpurin; sequel to the Researches on the Colouring-matters of Madder. By A. ROSENSTIEHL (*Compt. rend.*, lxxxiv, 1092—1094).—The author has already shown (p. 59 of this volume), that when pseudopurpurin is heated to 180°, it evolves CO_2, and becomes converted into purpurin. This decomposition would indicate the formula $C_{15}H_8O_7$ for pseudopurpurin, but the analysis gave results slightly different from those obtained by calculation, and he then stated that the difference might be due to the presence of purpurin. The object of the present paper is to confirm this opinion, and to give the analysis and properties of pure pseudopurpurin. By using the dyeing-test, the author finds that the pseudopurpurin prepared according to Schützenberger and Schiffart's method, still contains a little purpurin. He then prepared the sodium salt by the use of sodium carbonate, and on treating the aqueous solution of this salt with acid, obtained a finely-divided precipitate, which was levigated in cold alcohol. The first portions are coloured brown, and still contain purpurin, while the latter are of a red colour, and contain pseudo-purpurin, as proved by the dyeing-test. For 100 grams of substance, 20 litres of alcohol are used. The analysis of the substance dried at 100° in a vacuum gave—

	Found.		Calculated.	Schützenberger.
C	60·36	60·15	60·00	61·00
H	2·68	2·80	2·66	3·00

the formula taken for calculation was $C_{15}H_8O_7$.

The author thinks that pseudo-purpurin is an acid similar to salicylic acid, as it also is decomposed by heat into CO_2 and phenol; but he has as yet been unable to produce pseudo-purpurin synthetically by acting on the alkaline-derivative of purpurin with carbonic acid; he is continuing these researches. He has obtained pseudo-purpurin in large crystals by leaving a solution of the sodium-salt in alcohol and water to evaporate spontaneously. J. M. T.

Ethylterpene. By V. MEYER and C. PETRI (*Deut. Chem. Ges. Ber.*, x, 990—991).—Meyer and Spitzer obtained by the action of sodium on a mixture of ethyl iodide and monochloroterpene (camphor chloride) a crystallised hydrocarbon, which they believed to be ethylterpene, $C_{10}H_{15}.C_2H_5$ (this *Journal*, 1876, ii, 514). The authors tried to obtain a homologue by using propyl-iodide in the place of the ethyl-compound, but the product was found to be identical with the supposed ethylterpene, which, as the analysis and determination of the vapour-density showed, is nothing but a crystalline modification of terpene, being formed by the substitution of hydrogen for the chlorine, just as by the action of sodium on dry bromobenzene a considerable quantity of benzene is produced. C. S.

Rotatory Power of the Camphols. By J. DE MONTGOLFIER (*Compt. rend.*, lxxxiv, 445—447).—The rotatory power of certain specimens of borneol was found to be greatly increased by etherification and subsequent saponification, the increase depending partly upon the acid employed. Thus, a borneol feebly right-handed, + 1·42°, exhibited, after etherification with benzoic acid at 200°, and regeneration, a rotatory power of + 23·18°. A similar experiment at 275°, gave an increase of only + 12°; in this latter instance, an examination of the borneol showed that some inactive product had been formed; otherwise, the rule seemed to be that the higher the temperature at which the etherification took place, the greater the increase of rotatory power.

Acetic acid acts in a similar manner, thus:—

Rotatory power of original borneol	+ 10°.
,, ,, of regenerated borneol after the action of glacial acetic acid	+ 20°.
,, ,, after the action of ordinary acetic acid. .	+ 26°.

The action of heat alone also increases the rotatory power. A borneol, + 22°, derived from camphor, became + 30° after 10 hours' heating to 350°. Again, a camphol which was + 10°, rose to + 19° after 20 hours' heating at the same temperature; in this case, also, a small quantity of inactive or lævorotatory product was formed. Since camphols of feeble rotatory power are thus capable of being transformed into powerfully active substances by various reagents, the author thinks that they should be regarded as originally mixtures of two isomerides, one being right-handed and the other left-handed, but of unequal stability; indeed, it is possible to prepare from camphor, by means of sodium and carbon dioxide, camphols which are wholly and powerfully lævorotatory, as much as —24°, —21°, and —23°. Such products, however, have a very great tendency to become right-handed, and etherification or the action of heat slowly converts them. They do not correspond with any particular lævorotatory camphor, for on oxidation, they reproduce the original camphor with its characteristic dextro-rotatory power. A right-handed borneol or camphol is not capable of being converted into a left-handed one, so that when a mixture of the two is heated, it is the left-handed only that is affected; it will be seen, also, that during the conversion of a specimen, a point of neutrality can be obtained, at which the liquid no longer acts upon polarised light.

The rotatory power of natural borneol is + 37° or + 42°, for the sensitive or transition-tint. Biot gives + 33·4° for the transition-tint, but the author considers his own number to be the correct one; moreover, since artificial borneol has exactly the same rotatory power, it is supposed to be identical with the natural product. J. W.

Preparation of Betaïne. By R. FRÜHLING and J. SCHULZ (*Deut. Chem. Ges. Ber.*, x, 1070—1073).—The mother-liquors after treatment of beet molasses by the Scheibler-Seiferth process, being almost free from sugar, form an excellent material for the investigation of the organic compounds contained in the molasses. The alkaline solution, after being nearly neutralised with sulphuric acid, was evaporated, the potassium sulphate being removed as it crystallised out: it was then treated with alcohol and sufficient sulphuric acid to precipitate all the potassium and calcium in the form of sulphates. The alcoholic solution containing the acids originally present as salts in the molasses, and other organic compounds, including the betaïne, yielded formic acid on distillation; the residue, evaporated to dryness at 100°, and exhausted with absolute alcohol, gave a brown liquid, from which the betaïne was precipitated as hydrochloride, $C_5H_{11}NO_2.HCl$, in the crystalline state, by nearly saturating it with dry hydrochloric acid, the hydrochloride being but very slightly soluble in alcohol saturated with hydrochloric acid. This method the authors consider preferable to that of Scheibler or of Liebreich. The free base may be obtained in deliquescent crystals by decomposing the hydrochloride with silver oxide in the usual way. The authors are engaged in an examination of the acids accompanying the betaïne in the molasses.
C. E. G.

Extraction of Caffeine from Guaraná. By FRANCIS V. GREENE (*Pharm. J. Trans.* [3], viii, 87).—Instead of employing Stenhouse's method (*Pharm. J. Trans.* [1], xvi, 212), the author recommends the following:—Powdered guaraná is mixed with three times its weight of finely divided litharge, and boiled in distilled water until, on leaving it to cool, the insoluble portion rapidly subsides. The cool, clear liquid is then decanted through a filter, and the residue washed with boiling water, until the washings produce no precipitate with phosphomolybdic acid, or platinum-chloride. The small amount of lead in the filtrate is then precipitated by sulphuretted hydrogen, and the solution on evaporation yields colourless crystals of caffeine, which may be recrystallised from alcohol. E. W. P.

Crystalline Form of Brucine. By E. SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 838).—This paper is accompanied with a drawing, and measurements of angles are given, from which it appears that brucine forms monoclinic plates. C. S.

Preparation and Composition of Emetine. By J. LEFORT and F. WURTZ (*Compt. rend.*, lxxxiv, 1299).—When extract of ipecacuanha is dissolved in water and a concentrated solution of potassium nitrate added, a thick mass is produced, consisting of emetine nitrate. It is washed with water, dissolved in alcohol, and the solution poured into milk of lime. The mixture is evaporated to dryness and digested with ether, which dissolves out the emetine, leaving it as a yellowish mass on evaporation. On dissolving this mass in sulphuric acid, and pouring the solution into dilute ammonia, the alkaloïd is obtained as a white precipitate, which is dissolved in alcohol, from which it separates in minute radiate groups of needles. By analysis it gave numbers leading to the formula $C_{28}H_{40}N_2O_3$;* Glénard obtained the formula $C_{30}N_2H_{44}O_4$.

Pure emetine nitrate was prepared, and was found to have the formula $C_{28}N_2H_{40}O_5.NO_3H$; this, in conjunction with Glénard's results, shows that emetine does not form basic salts. C. W. W.

Critical Notes on Muscarine and some Allied Bases. By C. T. KINGZETT (*Pharm. J. Trans.* [3], vii, 998).—The author passes in review the various statements concerning the nitrogenous base, $C_5H_{15}NO_2$, obtained by Diakonow, and does not consider that this formula is correct, but that it should be $C_5H_{13}NO$, although it is possible that as a hydrate it would have the composition, $C_5H_{13}NO.H_2O$. Neither does he consider muscarine isomeric with betaine. The reasons are given in detail. E. W. P.

Sclerotic Acid, the Active Principle of Ergot. (*Pharm. J. Trans.* [3], viii, 106.)—To obtain pure sclerotic acid, very finely powdered ergot is exhausted with distilled water, the solution concentrated in a vacuum, and the residuary liquid mixed with an equal volume of 95 per cent. alcohol. This causes the precipitation of a peculiar slimy substance, *scleromucin*, together with a portion of the salts and the greater part of the suspended fatty matter. The mixture having been allowed to stand on ice for 24 or 48 hours, it is filtered, and the filtrate mixed with a further quantity of 95 per cent. alcohol, sufficient to precipitate all the sclerotic acid in combination with the bases (chiefly as calcium sclerotate). The separation of the precipitate is promoted as before by placing the mixture on ice for some days. This causes the deposited mass, which has a brownish colour, to adhere firmly to the walls of the vessel, so as to permit the supernatant liquid to be easily poured off. The precipitate is kneaded with alcohol of 80 per cent., and immediately afterwards dissolved in a sufficient quantity of 40 per cent. alcohol, when the remainder of the scleromucin and another larger

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* This is printed $C_{28}N_2H_{40}O_5$ in the formula for emetine nitrate, and as no data are given, it is impossible to tell which is correct.—C. W. W.

portion of the foreign salts are left behind. The filtered liquid is now mixed with absolute alcohol, whereby sclerotic acid is precipitated in conjunction with certain bases and other substances. The impure product, when carefully dried over sulphuric acid, was found on analysis to contain 8·5 per cent. of potassium, about 0·36 per cent. calcium, 4·3 per cent. sodium, 2·74 per cent. phosphoric acid, and 3·4 per cent. silicic acid, or altogether, 12·9 per cent. of ash. By further precipitation with absolute alcohol containing hydrochloric acid, sclerotic acid may be prepared containing only 2 per cent. of ash. Sclerotic acid thus obtained is odourless, tasteless, hygroscopic, but not deliquescent, and has a faint acid reaction. Boiling nitric acid of 1·200 spec. gr. produces a little picric and oxalic acid, and a new substance, which assumes a bright yellow colour on adding ammonia or other alkalis. More concentrated nitric acid converts it into picric, oxalic, mucic, tartaric, and aposorbic acids. It is not a glucoside; nor does it lose its effectiveness on the addition of dilute sulphuric or hydrochloric acids; on the contrary, the latter appears to intensify its effects. Boiling alcohol, in presence of sulphuric acid, extracts it from ergot in small quantities, cold alcohol not at all. It is therefore possible, by means of cold alcohol and sulphuric acid, to abstract a portion of the colouring matter from ergot, before extracting the sclerotic acid with water.
E. W. P.

Chlorophyll. By E. Fremy (*Compt. rend.*, lxxxiv, 983—988).—In this, his third communication on the subject, the author continues his examination of the two distinct substances which he has found to co-exist in the green colouring matter of leaves. The one of these—a yellow substance, called by the author *phylloxanthin*—is extracted from chlorophyll by alcohol of 62°, which leaves undissolved the other body, a bluish-green substance, to which the name of *phyllocyanic acid* is given. This substance is insoluble in alcohol of 62°, but is dissolved by alcohol of 70°. When also an alcoholic solution of chlorophyll is treated with a mixture of hydrochloric acid and ether, the ether dissolves out the phylloxanthin, and acquires a yellow colour, while the hydrochloric acid dissolves the phyllocyanic acid, and acquires a beautiful blue tint. If to a solution of chlorophyll in alcohol a few drops of baryta-water be added, a deep green barium salt of phyllocyanic acid is precipitated, whilst the alcohol acquires a fine golden-yellow colour from the phyllocyanic acid that remains in solution. The author now sees reason to believe that these two coloured substances exist in chlorophyll, in a state of simple admixture. The green colouring matter he has found contains potash, and therefore he terms it phyllocyanate of potassium. He was, however, unable by any means to isolate phyllocyanic acid, although he produced the potassium compound synthetically by double decomposition; and this was found to possess the spectroscopic and other properties of the green substance extracted from leaves by alcohol.
R. R.

Change of Colour in Chlorophyll. By A. Trécul (*Compt. rend.*, lxxxiv, 989).—The paper records some microscopical observations on changes of colour in the granules of chlorophyll, which the author has seen to pass in some cases from green to blue, and in other cases from green to orange-red. R. R.

Decomposition of Gelatin and Albumin by Pancreas Ferments in Absence of Air. By J. JEANNERET (*J. pr. Chem.* [2], xv, 353—390).—The author's conclusions, based on an extended series of experiments, are as follows:—

1. Decomposition of substances containing nitrogen, and of carbohydrates, by means of the bacteria of the pancreas, is possible in absence of air.
2. The process is, however, much slower when air is absent than under the ordinary conditions.
3. The more simple chemical compounds produced by the decomposition are the same, whether air is present or absent. Tyrosine was formed from albumin, after 29 days' action, in absence of air, and leucine from gelatin, after 11 days' action. These substances were not found after the same lapse of time when the decomposition proceeded in presence of air.
4. The gases produced in the decomposition of gelatin are almost wholly absorbed by caustic potash.
5. The amount of carbon dioxide produced in the decomposition of albumin and gelatin increases from day to day, as the action proceeds.
6. The pancreas bacteria are produced, and continue to exist, in absence of air; for their complete activity nitrogen compounds must be present. M. M. P. M.

Physiological Chemistry.

Absorption of Carbon Dioxide by Blood. By SETSCHENOFF (*Deut. Chem. Ges. Ber.*, x, 972).—From experiments on the blood of calves, sheep, horses, and dogs, it is inferred that the solubility-coefficient of carbon dioxide in serum is the same as in a dilute solution of a mixture of carbonate and phosphate of sodium, but that it varies with atmospheric pressure to a much greater extent than in the case of a solution of carbon dioxide in sodium carbonate, this being due to the presence of the alkalis in the blood in the form of albuminates (probably paraglobulinates), readily decomposed by carbonic acid, or decomposing alkaline carbonates by the reciprocal action, according to the pressure, increase of pressure bringing about the former, and decrease the latter result; thus, sodium carbonate is decomposed by albumin in a vacuum. The solubility of carbon dioxide in the red blood cellules (as free as possible from serum) is much greater than in water or serum, and is more regularly influenced by pressure and temperature, being at the temperature of the blood (37—37·5°), closely in accordance with Dalton's law, whence it appears probable that the bodies retaining the carbon dioxide are much less easily decomposed by fluctuations of temperature and pressure than the serum albuminates.

The normal amount of carbon dioxide in the capillaries corresponds with an absorption at 37—37·5°, and 50 mm. pressure; about one-sixth of this amount is due to the corpuscles, the rest being only lightly combined in the serum, and easily diffusible, wherefore it passes out into the air passages in the lungs on breathing; this outward passage must be more easy into an atmosphere containing oxygen than into one indifferent to hæmoglobin, or into a vacuum, whilst the oxygenised hæmoglobin must retain oxygen with less force in the capillaries. C. R. A. W.

Acidity of Human Gastric Juice. Observations on Digestion, made through the Agency of a Gastric Fistula. By CH. RICHET (*Compt. rend.*, lxxxiv, 450—452).—The operation of gastrotomy having been successfully performed upon a patient suffering from complete closure of the œsophagus, an opportunity offered for studying the operations of digestion in the human subject, by making use of the fistulous opening for withdrawing portions of the contents of the stomach. So complete was the stoppage of the œsophagus, that no saliva whatever passed into the stomach. A piece of sugar, impregnated with potassium ferrocyanide, and allowed to dissolve in the mouth, could not be detected in the liquids of the stomach by the prussian-blue test.

The gastric juice, thus free from saliva, was obtained pure by washing out the stomach with distilled water, and then placing some sapid substance in the mouth; this by a reflex action provoked a relatively abundant secretion of pure gastric juice. It is a colourless liquid, viscid, yet easily filterable, having little odour, and not putrefying spontaneously. The length of time that food remains in the stomach varies from three to four hours, for such aliments as starch, fat, or flesh proper; the digestion of milk lasts only about an hour and a half to two hours, while alcohol and water are still more rapidly absorbed, no trace of them being left at the end of 35 to 45 minutes.

The physiological inquiry to which the author paid particular attention was the determination of the acidity of the stomach under varying conditions, and the following facts were ascertained. The mean acidity of the gastric juice, whether pure or mixed with food, is nearly equivalent to 1·7 gram of hydrochloric acid per 1000 grams of liquid. The acidity never fell below 0·5, nor rose higher than 3·2 grams.

The quantity of liquid found in the stomach has no influence on its acidity; the latter is almost invariable, whether the stomach be nearly empty or very full.

Wine and alcohol increase the acidity, while cane-sugar diminishes it.

If acid or alkaline liquids are injected into the stomach, the gastric juice reassumes its normal acidity in about one hour.

The gastric juice is more acid during digestion than when digestion is not proceeding, and the acidity increases towards the end of the operation of digestion.

Since the stomach is generally empty at the end of four hours, and hunger does not supervene till about six hours after a meal, it would seem that hunger does not result solely from emptiness of the stomach. This observation, the author remarks, is in contradiction to the opinion of some physiologists; at the same time he is not able to offer any further solution of the question. J. W.

Remarks on Bastian's Archibiosis. By D. MÜLLER (*Deut. Chem. Ges. Ber.*, x, 776—780).—The author has repeated Bastian's experiments with every attention to accuracy, but has not been able to discover a trace of archibiosis in urine previously boiled, then neutralised with potash, and heated to 50°. The retorts containing the urine were, after boiling, sealed up, when on cooling the little sealed tubes containing the potash broke. When a temperature of 50° was kept up for a week, no bacteria made their appearance. When oxygen and hydrogen were developed by electrolysis in the urine previously boiled, and then allowed to cool, no life made its appearance. Air previously passed through concentrated sulphuric acid gave negative results on passing through the urine. The boiled urine was now furnished with air, previously filtered through purified cotton-wool: here also negative results were obtained, the urine remaining quite free from bacteria. Two retorts were partly filled with unboiled urine, two others with boiled urine. All these portions of liquid were almost completely neutralised with unboiled potash, covered with blotting paper, and exposed to a temperature of 50° for 8 days (192 hours). There was then no visible reaction. The retorts were now sealed up. Eight days afterwards those retorts whose contents had not been boiled began to become turbid. Warming for 48 hours caused no further change. After standing longer, some salt was deposited, and on microscopical examination bacteria were found in quantities, singly, linked together, and in threads of various dimensions. Bastian has declared that only the exact quantity of potash must be used for the nearly complete neutralisation of the urine, and that the smallest excess would prevent the desired action. Pasteur does not share the views of Bastian, and the latter states that Pasteur's point of saturation and temperature employed were different from his. The present researches of the author were undertaken with every precaution which Bastian employed in his, and they have led him to the positive certainty that no such thing as *Generatio aequivoca* occurs in solutions of this kind free from germs, and that even in such germ-containing solutions a temperature of 50° is not suited for the development of bacteria. In face of the difficulties attendant on the case of urine, the author employed another organic solution, viz., a neutral broth. One part by weight of ox-flesh from a muscular part, and as free from fat as possible, was cut up small, and boiled with distilled water for two hours, so that nearly three parts by weight of solution remained. This solution was filtered boiling, through a threefold filter, and then transferred perfectly clear by means of a pipette to the retorts used for the investigation. In two of these retorts little tubes were placed, containing neutral potassium tartrate solution; the third remained without addition. Three other retorts were also similarly arranged. The broth was slightly acid. Two of the retorts contained little tubes with potash-solution for the nearly complete neutralisation of the flesh-extractive solutions. After boiling the contents of the retorts for five minutes, the ends were sealed up, and the solution cooled. In two retorts the tubes were broken. and all six retorts were exposed for 72 hours to a temperature of 50°. No trace of bacteria. The tubes in the other two retorts were now broken, and these were again exposed to a temperature of 50°, but with the like result.

For all the investigations above detailed morning urine was employed, which was taken in a carefully cleansed bottle, with well fitting stopper, and so that the bottle when stoppered was quite full.

W. S.

On the Non-existence of "Urinary Mucus." By C. MEHU (*J. Pharm. Chim.* [4], xxv, 106—112).—In ordinary language the "mucus of the urine" designates the deposit which appears in urine left at rest, and usually collects at the bottom of the vessel, rarely remaining in suspension. This usually translucent sediment is commonly composed only of epithelial cells from the bladder, and especially of epithelial detritus from different parts of the urinary passage. Urates and uric acid are also often present, and in the case of invalids, it often contains *leucocytes*, blood, semen, calcium and magnesium phosphates, confervæ, vibrios, and anatomical elements of the kidney. The "urinary mucus" is then said to be abundant; in fact, this word "mucus" is used to designate so many different things, that it becomes necessary to define it for each particular case.

The liquids secreted by the glands of the urethra would be removed by the first portion of the urine; the latter portions of the urine, however, give as much deposit as the first: hence these secretions do not constitute the "mucus."

This visible sediment is constant, but it is not mucus, for the principle, termed "mucin" by Scherer, is perfectly definite and easy to characterise. It gives a viscous consistency and a power of frothing to water; it is *invisible* when dissolved in water, not coagulable by heat alone, precipitated completely by acetic acid in the cold, and not soluble in excess of the reagent; mineral acids precipitate mucin, but an excess of acid dissolves the precipitate; alcohol also precipitates it. Mucin can be obtained in a pure state from the *Ranunculus palustris*, and from the healthy human knee-joint. Mucin is never present in the most viscous urine; and the application of the term "mucus" to a deposit of varying composition is evidently unscientific. The different substances which constitute this deposit are pus (which gives the most copious deposit), semen, blood, organic detritus, phosphates, urates, or a mixture of these different substances.

Pus if left at rest separates into two layers, a white inferior one of *leucocytes*, an upper yellow or greenish-yellow one, either fluid or thick, of *serum*. The *leucocyte* is characteristic of pus, as the spermatozoïd is of semen, and hematin of blood.

The *leucocyte* differs in appearance with the acid or alkaline reaction of the urine, and with the length of time it has been in the urine: in a very alkaline urine it loses its form and alters its natural size, is altogether changed in appearance, and after some time the granulations alone are distinguishable.

The *serum* includes two principal organic elements, *serin* and *pyin*.

Serin is the albuminous constituent of the blood; it is coagulable by heat, not precipitable by acetic acid, coagulable by nitric acid. Filtered urine containing pus owes its property of becoming troubled with albuminous flocks by boiling, chiefly to the serin. *Pyin*, like mucin, is precipitated by acetic acid; but mucin, precipitated by a mineral acid, differs from pyin in being soluble in excess of the acid. Pyin does not yield a viscous aqueous solution as mucin does: it is precipitable by mercuric chloride and neutral lead acetate, but these reactions are usually not applicable, on account of the simultaneous presence of serin.

Mucin in solution is not coagulable by heat, whilst ebullition coagulates serin and pyin without addition of acetic acid, if the serum has not become too alkaline by putrefaction. Hence any liquid containing pus, when filtered and limpid, becomes turbid on addition of acetic acid. This test for pus is very delicate if time is allowed for the precipitate to form when mere traces of pus are present. The detection of pus by this test is much less tedious than the search for *leucocytes* under the microscope.

But urine in which blood-globules have remained for some time, is also troubled by acetic acid; this is especially the case if the urine is ammoniacal, and if endosmose is assisted by low density of the urine. Semen, and even epithelial scales which have long remained in alkaline urine, also give rise to a precipitate with acetic acid. Hence acetic acid indicates the presence of anatomical elements only, such as leucocytes, spermatozoïds, hæmatin-cells, and numerous epithelial cells; but in the great majority of cases leucocytes are indicated by it.

The absence of mucin in urine is proved by suspending the precipitate produced by acetic acid in water, and adding a mineral acid; the precipitate remains undissolved.

Urine containing much pus rapidly putrefies, becomes alkaline by formation of ammonium carbonate, and then yields so abundant a deposit as to become viscous and often semi-solid; crystals of ammonium magnesium phosphate are found in this deposit. Leucocytes shaken with ammonia give a similar viscous liquid due to the solution of the *leucocytes*. Such viscous urine is generally called "highly charged with *mucus*," where by mucus must be understood pus.

The existence of *urinary mucus* as a special secretion is, then, totally denied: the so-called *mucus* of urine is but a normal sediment of infinitely varying character and aspect. A mucus contains mucin; urine contains no mucin: and mucin in solution offers nothing visible to the eye. Epithelial detritus is wrongly termed mucus. F. C.

Chemistry of Vegetable Physiology and Agriculture.

Functions of the Leaf and Stomates in Promoting Exchange of Gases between Plants and the Atmosphere. By A. Merget (*Compt. rend.*, lxxxiv, 376—379).—According to Unger and Sachs, the stomates of a plant are the normal openings through which pass, in both directions, those gases which are continually exchanged between the plant and the atmosphere. According to M. Barthélemy, the stomates act rather as safety-valves, which open to permit the passage of nitrogen outwards, but do not prevent the entrance of atmospheric air: the transfusion of oxygen and carbon dioxide he explains by cuticular dialysis.

In order to resolve, if possible, these conflicting assertions, the author has undertaken some experiments. Using mercurial vapour, which is incapable of solution in water and of diffusion by dialysis, he has shown that it penetrates readily, even to the deepest cells of the parenchymatous tissue of a plant; that under those circumstances it attacks and destroys the cellular protoplasm, whereby its action can be traced; and that its toxic effect is prevented if the stomates be artificially closed previous to the introduction of the leaf or plant into the mercurial vapour. Again, that if mercury be injected into the canals of the petiole of a leaf, and the latter be then pressed between folds of paper rendered sensitive by ammoniacal silver nitrate solution, an impression of the leaf is obtained upon one side of the paper only, when operating on leaves containing stomates upon one surface only, thus distinctly showing that the vapour must also be capable of passing *out* through these ostioles.

In a similar manner by enclosing a distomatous leaf between sensitive paper, and placing on one side a plate of amalgamated copper, an impression of both sides of the leaf can be obtained, the mercurial vapour entering by the stomates on the upper face, and passing out by those on the lower.

Any gas can be substituted for mercurial vapours in these experiments, if it is capable of being readily detected, or if its action can be traced by an alteration of colour in the tissue. The author has successfully used ammonia, sulphurous anhydride, hydrogen sulphide, cyanogen, chlorine, the vapour of iodine and bromine, &c., and has obtained results which in every instance confirm the hypothesis of Unger and Sachs. J. W.

Decomposition of Carbonic Acid in the Solar Spectrum by the Green parts of Plants. By C. TIMIRIAZEFF (*Compt. rend.*, lxxxiv, 1236).—Five eudiometers were arranged in a darkened room in such a manner that each was illuminated by a different part of the spectrum. The first was in the extreme red; the second in the part of the red corresponding to the band characteristic of chlorophyll; the third in the orange; the fourth in the yellow; and the fifth in the green; it was thought useless to experiment on the effect of the blue rays and those following them.

These eudiometers were filled, over mercury, with atmospheric air containing 5 per cent. of carbonic acid, and in each was placed a piece (about 10 cm. sq.) of bamboo leaf. They were exposed to the light for six to ten hours.

After the experiment the gas was removed from the tubes and analysed. Six series of experiments gave perfectly concordant results.

The greatest amount of decomposition of the carbonic acid took place in the tube corresponding with the position of the absorption-band characteristic of chlorophyll; in the orange, yellow, and green the amount gradually decreased, while in the extreme red, not only was there no decomposition, but carbonic acid was produced by the respiration of the leaf. C. W. W.

Physiological Relations of Asparagine. By L. PORTES (*Compt. rend.*, lxxxiv, 1401—1404).—The author advances an hypothesis to account for the presence of asparagine in almonds, and in the germinal parts of other plants. He supposes that at the period of most active growth the albuminoïd matters of the plant are split up—one part, including the nitrogen, forming asparagine, while the remainder enters into the composition of cellulose, dextrin, &c. R. R.

Chemical Examination of Mistletoe. By H. GRANDEAU and A. BOUTON (*Compt. rend.*, lxxxiv, 500—502).—Having previously shown, by a comparison of the composition of the ash of mistletoe grown upon different trees, that this parasite assimilates the mineral constituents of the plant on which it lives, in very unequal proportions, and that these proportions bear no direct relation to the ash of the plant itself, the authors have proceeded to investigate the proximate composition of the branches, leaves, and fruits of the mistletoe from the oak, willow, dogwood, and pear-tree, and to determine the relative nutritive value of the same when employed for feeding cattle. From the numerical results, which are given in full, the following facts may be gathered:—

That while the composition of the leaf and branch of the same specimen is nearly identical, their percentage of nitrogenous constituents, when compared with that of the same parts of plants from different sources, varies very greatly, as much as 25·66 to 13·02 per cent. for the leaves, and 20·4 to 7 25 per cent. for the branches.

That the fruits of pear-tree and dog-wood mistletoe are comparatively poor in nitrogenous substances.

That the percentage of non-nitrogenous extractive varies greatly in mistletoes from different sources (53·20 to 39·94 per cent.), while the proportions of gum and resinous matter are tolerably constant.

That the percentage of ash bears no well-marked relation in any way to the nutritive value of the specimen. The authors are of opinion that the composition of the green parts of the mistletoe, as shown by their analyses, perfectly justifies the use which is made of it in some districts as an article of fodder. They think that the mistletoe of the oak may rank in nutritive value with ordinary grass and clover: that the leaves of the dog-wood and pear-tree mistletoe are about equal to good hay; and that their branches may be compared with pea-straw, bean-straw, or the chaff of cereals. J. W.

The Distribution of the Alkaloïds in Cinchona Trees. By DAVID HOWARD (*Pharm. J. Trans.* [3], viii, 1).—On comparing the amount of the different alkaloïds obtained from the bark of the roots, stem, and branches of *Cinchona succirubra*, *C. officinalis*, and others, it is found that, although in each species the absolute quantities are different, the bark of the root produces, in greatly increased proportions, the dextrogyrate alkaloïds, whereas the branches produce these in very diminished proportions, the amount of cinchonine and quinidine increasing as the root is approached, more rapidly than that of the quinine and cinchonidine. A table shows the exact proportions :—

	Branch.	Stem.	Root.	Root fibres.
Total alkaloïd	3·3	5·5	7·6	2·0
Composed of—				
Quinine	23·5	20·2	11·5	13·0
Quinidine	·6	·6	2·9	11·4
Cinchonidine......	25·3	23·6	19·9	11·7
Cinchonine.........	19·4	32·8	47·3	46·7
Amorphous	31·2	22·8	18·4	17·2

In the case of renewed barks, an increase in the yield of the alkaloïds is found, the increase of quinine and its isomerides being accompanied by a diminution of cinchonine and cinchonidine. E. W. P.

Agricultural Analyses. By A. VOELCKER (*Journ. Roy. Agri. Soc.*, 1877, 188—200).—The Peruvian guano from the Guanape and Macabi Islands being exhausted, southern deposits are now being worked. The present importations are from Pabillon de Pica, Independencia Bay, and the Lobos Islands; there are, apparently, three varieties of the first-named guano. Small quantities of African guano are also imported from Saldanhay Bay and the Ichaboe Islands.

	Pabillon de Pica.			Independencia Bay.	Lobos Islands.	Saldanhay Bay.	Ichaboe Islands.
	Pabillon.	Huanillos.	Punta de Lobos.				
Number of analyses....	5.	4.	4.	4.	4.	1.	1.
Water	11·59	18·01	8·11	8·69	19·96	22·25	17·01
Organic matter and ammonium salts	39·89	36·22	30·81	34·62	18·73	37·43	41·54
Phosphate of calcium..	26·98	24·81	35·96	20·13	42·59	18·24	20·18
Alkali salts	15·65	16·66	20·23	13·62	10·92	3·59	2·53
Sand	5·89	4·30	4·89	22·94	7·80	18·49	16·85
Nitrogen	8·79	7·77	5·95	7·89	3·55	9·29	10·07
Total phosphoric acid..	13·82	14·18	17·87	10·24	20·66	9·35	—
Soluble phosphoric acid	1·47	2·82	1·41	1·02	1·38	·99	—

The ancient deposits of Saldanhay Bay and the Ichaboe Islands were removed many years ago. By protecting the birds during the breeding season they have again multiplied in large numbers on the islands. The birds appear in June, and begin to lay as soon as sufficient dung has accumulated to form the nests. In March they leave the islands for three months. During this interval the guano is collected.

The following table shows the great variation in the composition of rice meal, and also the composition of the seeds of the locust bean. These seeds are very hard, and must be steamed before being given to cattle as food. The "carbo-hydrates" are in their case chiefly mucilage:—

	Rice Meal, I.	Rice Meal, II.	Seeds of Locust Beans.
Water	9·47	7·51	11·19
Albuminoïds......	6·56	12·37	5·94
Oil............	3·77	13·53	·97
Carbo-hydrates....	58·96	54·94	76·29
Fibre............	13·77	3·90	3·62
Ash	7·47	7·75	1·99

R. W.

Analytical Chemistry.

Quantitative Determination of Precipitates without Washing and Drying them. By Richard Popper (*Zeitschr. Anal. Chem.*, xvi, 157—171).—The author describes an improvement in the method of ascertaining the weight of a precipitate whose specific gravity is known, by weighing a specific gravity bottle first filled with water, and then again, after it has been filled with water and the well-washed precipitate. By this means the process of drying the precipitate is avoided. The author has further dispensed with the washing of the precipitate, by weighing it in the liquid in which it has been precipitated, and determining the specific gravity of this liquid by an additional weighing of the bottle filled therewith. The following formula for finding the weight of the precipitate is deduced:—

$$x = \frac{S}{S-s}(G-g).$$

in which x = the required weight of the precipitate,
S = the specific gravity of the precipitate,
s = the specific gravity of the solution in which the precipitate has been produced.
G = the weight of the specific gravity bottle filled with the solution containing the precipitate.
g = the weight of the bottle filled with the same solution alone.

To prove the accuracy of the method, the weight of the aluminium hydrate precipitate was determined, both by this method and the ordinary gravimetric process, and the results were sufficiently close to warrant the employment of the method at least for technical purposes. By the new method, in four analyses 10·73, 10·67, 10·70, and 10·59 per cent. of Al_2O_3 were found, and the mean of two gravimetric determinations made with the same alum was 10·72.

The mode of transferring the precipitate from the beaker to the bottle which was finally adopted was the following. After the precipitate had settled in the beaker, the supernatant liquid was drawn over by a syphon arrangement into the wash-bottle; the first portions, after being used for rinsing out the wash-bottle, were rejected. The rest of the liquid was then syphoned over into the wash-bottle, and with a part of it the precipitate was rinsed into the specific gravity bottle, and the bottle filled, the remainder being employed for determining the specific gravity of the solution. The precautions requisite to secure accuracy in an ordinary specific gravity determination must of course be attended to, and a few others are mentioned as the result of the author's experience. The precipitation must not take place in very strong solutions, and the precipitate must be removed to the bottle as soon as possible, else it is liable to attract salts from the solution, and thus rise in specific gravity. The specific gravity bottle should hold not less than 30 c.c., and for convenience in drying should have no lip. Several examples of analyses are given, to which the new method is specially suitable.

The determination of the specific gravity of a precipitate is made by first weighing the specific gravity bottle alone, then when filled with water containing the well-washed precipitate. The precipitate from the bottle is then carefully thrown upon a filter and weighed. Then the weight of the bottle containing the precipitate and water = the weight of the bottle filled with water $+ N - \frac{N}{S}$, (where N = the weight of the precipitate, and S its specific gravity). Subtracting then from the weight of the bottle containing the precipitate and water, its weight when containing water alone, we get:—

$N - \frac{N}{S}$; let this equal M, then $S = \frac{N}{N - M}$.

The specific gravity of the precipitate did not appreciably vary when formed in dilute and in strong solutions. F. C.

A New Apparatus for Heating Substances in Sealed Tubes under High Pressure suitable for Analytical and Synthetical Operations. By C. O. Cech (*Zeitschr. Anal. Chem.*, xvi, 320—323). —After giving a brief description of the present form of digesters used in laboratories for heating substances enclosed in sealed tubes to a certain temperature, the author describes his improved apparatus, which is said to overcome all the difficulties and dangers to which chemists are often exposed by using the old form of ovens. The oven is made of strong sheet iron in the form of a cylinder, and riveted on one side only, while the old digesters consist of square iron boxes riveted in four places. These cylinders not only resist the high pressure more effectually than square boxes, but they also have the great advantage of holding a larger number of tubes to be heated. By fixing this oven in the wall which leads to the chimney, all explosions which may occur during heating will thus take place in the flue. D. B.

A new Indicator for Titrating Alkalis and Acids. By E. LUCK (*Zeitschr. Anal. Chem.*, xvi, 332—333).—*Phenol-phthalein*, a body discovered a few years ago by Baeyer, and easily prepared by heating phenol with phthalic anhydride and sulphuric acid, is perfectly colourless in a dilute aqueous or acidulated solution, but assumes a deep purple colour on adding the slightest excess of alkali. One part of phenol-phthalein in 100,000 parts of water is turned red by the least traces of alkali, and the coloration is destroyed by a minimum of acid. For practical purposes one part of phenol-phthalein is dissolved in 30 parts of alcohol. To about 80—100 c.c. of the solution to be titrated 1 or 2 drops (no more) of the indicator are added. The smallest drop of a normal alkali or acid solution is more than sufficient to bring about the conversion of the neutral into the alkaline or acid reaction.

D. B.

Detection of Carbon Monoxide. By H. W. VOGEL (*Deut. Chem. Ges. Ber.*, x, 792—795).—The endeavour was made to use the long known spectrum reaction of blood more or less impregnated with carbon monoxide, for the discovery of small quantities of this gas in gaseous mixtures containing it. The behaviour of carbonyl-hæmoglobin has been long used in order to certify cases of poisoning with carbon monoxide, but the idea that carbon monoxide might be detected in the atmosphere of rooms by means of blood does not appear to have been thought worthy of testing. The author has found that the recognition of small quantities of carbon monoxide in atmospheric air by means of blood, can be rendered quite easy, in spite of the presence of oxygen, and that the process leaves nothing to wish for in certainty, simplicity, and delicacy. To detect the presence of carbon monoxide in the air of a room, a flask containing 100 c.c. of water is emptied out in the room, and into this flask 2—3 c.c. of blood very largely diluted with water are poured. This blood-solution must possess only a faint shade of red. The bottle or flask is now shaken for only one minute, when the carbon monoxide causes the known reaction and alteration of colour. The latter appears more rose-coloured, the absorption bands appear a little paler, and more turned to the left, than is the case with normal blood. With very little practice certainty can be acquired, or this can immediately be attained by adding three to four drops of strong ammonium sulphide, which in blood free from carbon monoxide, as is known, causes the disappearance of both bands, and the substitution of one broad faint shadow, whilst with blood containing carbon monoxide, ammonium sulphide produces no optical change, the bands remaining as they were. To test the delicacy of the reaction, a mixture of carbon monoxide and dioxide was prepared according to the known method, with oxalic acid and sulphuric acid, and was used without separating the carbon dioxide. This was done, remembering that where carbon monoxide occurs in common air, there carbon dioxide also exists. 1 c.c. of this gaseous mixture was mixed with 60 c.c. of air in a graduated cylinder, and then shaken with about 2 c.c. of the above-mentioned very dilute blood for two minutes. The carbon monoxide reaction was then most unmistakeably obtained. Accordingly 0·8 per cent. by volume of carbon monoxide in atmospheric air can be detected with the utmost ease. 0·4 per cent. can likewise be detected by a practised spectroscopist, and by a novice even by taking a large quantity of air (500 c.c.), with about 3 c.c. of the dilute blood. For the experiment all that is necessary is a small drop of blood, a little ammonium sulphide, a pocket spectroscope, and a test-tube. The author has successfully experimented with blood preserved by means of salicylic acid for a week. It is recommended that the experiments should be conducted comparatively, with a sample of perfectly pure blood. A quantitative estimation has never been attempted, but no reason is known why a method should not be devised. The delicacy of the reaction is still further heightened by the removal of oxygen the presence of which, Liman has found, somewhat detracts therefrom.

W. S.

Determination of Dextrose and Levulose by an Indirect Method. By C. NEUBAUER (*Deut. Chem. Ges. Ber.*, x, 827—830).—If α is the angle of rotation, A the rotatory constant, and L the length of the tube, the amount of sugar in a litre is found by the equation $C = A\frac{\alpha}{L}$. This formula likewise enables us to calculate the rotatory angle of a solution containing a known percentage of sugar, and to determine the quantities of dextrose and levulose in a mixture. The results which the author obtained showed, however, that the quantities found did not agree with the calculated ones, because levulose has not the specific rotatory power —106 for yellow light, as generally assumed, but that of — 100, and its rotatory constant is therefore 1,000 at 14°, or the values for calculation are:—

Specific rotatory power of dextrose............	+ 53·1
" " " levulose............	— 100
Rotatory constant of dextrose	+ 1883·3
" " " levulose	— 1000
Difference of the two latter	2883·3

Now, supposing that must contains 8·6 per cent. levulose and 6·4 dextrose, we find by Fehling's method 15 per cent. of sugar, which, if present as levulose only, would require, in a tube of 100 mm. at 14°, a rotation of — 15°, while it is found to be — 5·202°. The difference is therefore — 9·798°, and from this we find the percentage of dextrose by the equation—

$$2888{\cdot}3 : 188{\cdot}3 :: 9{\cdot}798 : x$$

$$\therefore\ x = 6{\cdot}4.$$

C. S.

Determination of Acetic Acid. By C. JEHN (*Arch. Pharm.* [3], x, 414).—10 c.c. of the acid are caused to decompose sodium bicarbonate; the carbon dioxide produced is passed into a cylinder filled with water, and the displaced water flows into a measuring vessel. From the volume of water displaced, the volume of carbon dioxide is known, and the amount of acetic acid is calculated.

M. M. P. M.

Commercial Oxalic Acid contaminated with Sulphuric Acid. By O. BINDER (*Zeitschr. Anal. Chem.*, xvi, 334).—In analysing oxalate

of ammonium, the author found that it contained a large quantity of sulphuric acid. The oxalic acid used for the preparation of the former also contained sulphuric acid to the extent of 0·4 p.c. The acid was present in the free state, enclosed in the crystals, but also as acid sulphate. Wicke found the same contamination in oxalic acid in 1857.
D. B.

The Pharmacopœia Test of Quinine Sulphate. By B. H. PAUL (*Pharm. J. Trans.* [3], vii, 653).—The present pharmacopœia test for the presence of cinchinidine sulphate in quinine sulphate is not delicate enough, owing to the fact that the presence of quinine in large quantities increases the solubility of cinchonidine in ether. It is therefore recommended to boil 30 grains of quinine sulphate with 1½ fluid ounces of water. On cooling, the greater part of the quinine sulphate crystallises out, leaving the cinchonidine sulphate in solution; and to this solution the cinchonidine test may be applied. E. W. P.

Testing Beeswax for Resin. By E. SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 837).—The following modification of Donath's method gives the means of detecting even 1 per cent. of colophony in yellow beeswax. 5 grams are heated in a flask with 20—25 grams of nitric acid of sp. gr. 1·32—1·33, and boiled for one minute. The cold liquid is diluted with an equal volume of water and shaken with ammonia in excess. If the wax is pure the solution has a yellow colour, but if resin is present nitro-compounds are formed,. imparting to it a deep reddish-brown tint. C. S.

Estimation of Nitrous and Nitric Acids. By G. LUNGE (*Deut. Chem. Ges. Ber.*, x, 1073—1076).—1. *Estimation of Nitric Acid.*—The author finds that the estimation of nitric acid by oxidation of ferrous sulphate (Pelouze), determining the excess of the latter by permanganate, gives accurate results; he recommends adding 20 per cent. of its weight of sulphuric acid to the solution before heating with the nitrate to facilitate the oxidation. Siewert's method, reduction in alkaline solution by zinc and iron, gives low and variable results. Hager's modification and Schulze's process are also untrustworthy.

2. *Estimation of Nitrous Acid.*—The methods were tested on a solution of pure silver nitrite in sulphuric acid. Feldhaus' permanganate method gives good results, but the standard solution must not be too strong, and the nitrite solution should be added to it, not *vice versâ*, or there will be loss from the decomposition of the nitrous acid and escape of nitrogen dioxide. It is advisable to keep the solution at 40—50°, as at lower temperatures the reaction does not take place instantaneously, so that the point of decolorisation cannot be so accurately observed. Gerstenhöfer's modification of the bichromate method does not give equally good results, as it is difficult to observe the exact point when all the chromate is reduced. The other processes examined, namely, Siewert's, Hart's, and Crowder's, did not give accurate or constant results.

3. *Estimation of Nitrous and Nitric Acids.*—The nitrous acid in the mixture is first determined by oxidising it to nitric acid by standard permanganate, and then the total quantity of nitric acid present in the

solution is estimated by means of ferrous sulphate. The amount of nitric acid originally present is found by subtracting from the result that formed by the oxidation of the nitrous acid.

4. *Analysis of a "Nitrose."*—This "nitrose" (sulphuric acid used to absorb nitrous fumes) from a soda factory, had a density of 1·691 at 15°, and was saturated. It contained 4·13 grams N_2O_3 in 100 c.c., but no nitric acid. This result differs from those obtained by Winkler, who found nitric acid present; this, however, was probably due to the analytical method employed; for Winkler added the permanganate solution to the nitrose, and experiments made by the author with a solution of silver nitrite in sulphuric acid showed that in this case not only was nitric acid formed, but that nitrogen escapes as dioxide. It should be stated, however, that Kolbe found nitric acid in nitrose, although the nitrous acid determinations were made by adding the solution to the permanganate. C. E. G.

Various Methods for Determining Nitric Acid. By J. M. Eder (*Zeitschr. Anal. Chem.*, xvi, 267—314).—The more generally used processes for the determination of nitric acid have been experimentally examined by the author. These processes he divides into two groups: 1. Those in which nitric acid is determined from a measurement of the amount of another substance which is oxidised by it. 2. Those in which the nitric acid is transformed into another nitrogen-compound, which compound is capable of being easily measured or weighed. Each group of processes is subdivided.

Group I.—A. Methods which depend upon the Oxidation of Ferrous Salts.—α. *The nitrate is decomposed by excess of ferrous salt, and the amount of residual unoxidised salt is measured.* Method of Pelouze, &c. The ferrous salt usually employed is the chloride. The process, as originally carried out, is open to several objections. The author has modified Fresenius's improvements as follows:—1·5 gram of very thin iron wire is dissolved in 30 to 40 c.c. of pure fuming hydrochloric acid, placed in a retort of about 200 c.c. capacity; the beak of the retort points upwards, at a moderately acute angle, and is connected with a U-tube, which contains water. Solution of the iron is hastened by applying a small flame to the retort. Throughout the entire process a stream of carbon dioxide is passed through the apparatus. When the iron is all dissolved, the solution is allowed to cool, the stream of CO_2 being maintained, the weighed quantity of nitrate contained in a small glass tube (equal to about 0·2 gram HNO_3) is then quickly passed into the retort through the neck; the heating is continued under the same conditions as before, until the liquid assumes the colour of ferric chloride; the whole is allowed to cool in a stream of CO_2; water is added in quantity; and the unoxidised iron is determined by titration with permanganate. The results are exceedingly good. If the CO_2 be generated in a flask, with a tube passing downwards for the reception of the acid, air always finds its way into the retort, and the results are unsatisfactory. The author recommends the use of Kipp's CO_2 apparatus. By carrying out the operation exactly as is now to be described, the author has obtained very good results with ferrous sulphate in place of chloride. The same apparatus is employed; the tube through which CO_2 enters the retort passes to the bottom of the liquid therein, and the lower extremity of this tube is drawn out to a fine point. The bubbles of CO_2 are thus reduced in size, and the whole of the nitric oxide is removed from the liquid by the passage of these bubbles. The iron wire is dissolved in excess of dilute sulphuric acid, strength 1 : 3 or 1 : 4. When the liquid in the retort has become cold, a small tube containing the nitrate is quickly passed, by means of a piece of platinum wire attached to it, through the tubulus of the retort, and the cork is replaced before the tube has touched the liquid: CO_2 is again passed through the apparatus for some time, after which, by slightly loosening the cork, the tube containing the nitrate is allowed to fall into the liquid. The whole is allowed to remain at the ordinary temperature for about an hour—this is essential—after which time the contents of the retort are heated to boiling, CO_2 being passed continuously into the retort, and the boiling continued till the liquid assumes the light yellow colour of ferric sulphate. After cooling, water is added (this may be omitted), and the unoxidised iron is determined by means of permanganate. The author also describes a slight modification of this process, allowing of the use of a flask in place of the retort, and of ammonio-ferrous sulphate in place of iron wire. Although the titration with permanganate is more trustworthy when sulphuric acid is employed than when hydrochloric acid is used, the author nevertheless thinks that the use of ferrous chloride is generally to be recommended in preference to that of ferrous sulphate. When the chloride is employed, no special concentration of acid is necessary: the nitric oxide is more readily expelled from the liquid, and the process is finished in a shorter time.

The final point in the titration with permanganate, when the sulphate is employed, is rendered more easy of determination by adding a little potassium sulphate to the liquid.

β. *The nitrate is decomposed by excess of ferrous salt, and the amount of ferric salt is directly determined.*—The process of Fresenius (*Zeitschr. Anal. Chem.*, i, 26) is slightly modified by the author. About 10 grams of ammonio-ferrous sulphate is dissolved in a flask, in about 50 c.c. of hydrochloric acid (sp. gr. 1·07), in a stream of CO_2. The tube through which the CO_2 enters, is drawn to a point; an exit-tube, somewhat trumpet-shaped, to admit of any liquid that may spirt finding its way back into the flask, passes downwards into water. After solution of the double salt, the nitrate is dropped in with the precautions already detailed, and the liquid is boiled until the nitric oxide is all expelled. The hot liquid is diluted with twice its own volume of water, excess of standard stannous chloride solution is run in, the whole is allowed to cool in a stream of CO_2, and the excess of tin is determined by means of a standardised iodine solution. This process is strongly recommended by the author.

γ. *The nitric acid is determined by titration with standard ferrous solution.*—This is the process of Grossart: it has been modified by Mohr. The author has carefully examined all proposed forms of the process, but has failed to obtain satisfactory results from any. The principal objections are:—

1. The final reaction is indefinite.

2. Nitric acid is lost by evaporation from the hot solution.

3. The reaction between nitric acid and ferrous sulphate is incomplete, unless the latter be in excess.

B. METHOD DEPENDING UPON THE OXIDATION OF CHROMIUM SALTS TO CHROMIC ACID.—This method gives most excellent results, provided atmospheric air is completely excluded from the apparatus, and no substances are present which are capable of forming insoluble chromates. Chlorides and sulphates exert no injurious effect upon the reaction. In the analysis of such a substance as lead nitrate by this process, the author recommends solution of the salt in water, precipitation of the lead by addition of sodium carbonate, filtration, and evaporation of the filtrate to dryness. He places the mixture of nitrate, chromium oxide, and soda in a boat—of platinum, if possible—which is then placed in a combustion-tube, fitted with an exit-tube passing a little way under the surface of water. Dry CO_2 is passed through the combustion-tube; the mixture is heated for ten minutes; the boat is withdrawn; the mass is dissolved in water; and the chromic acid is determined. The nitric oxide which escapes during the reaction may be determined, and in this way two analyses may be simultaneously performed.

Wagner's modification of the process, in which the mixture is fused in a crucible, has been tested by the author, but the results are so unsatisfactory that he cannot recommend the method, even for technical analyses.

GROUP II.—A. METHODS WHICH DEPEND UPON THE TRANSFORMATION OF THE NITRIC ACID INTO NITRIC OXIDE.—α. *The nitric oxide produced is re-transformed into nitric acid, which is then measured. The nitric acid is decomposed by means of ferrous chloride.* The process was originally brought forward by Schlösing (*J. pr. Chem.*, lxii, 142); Reichardt (*Zeitschr. Anal. Chem.*, ix, 23) modified the apparatus. The author employed the apparatus of the latter chemist; the nitric acid was determined by titration with $\frac{1}{10}$th normal soda solution. Some difficulty is often experienced in removing the whole of the nitric oxide from the solution in ferrous chloride. The author closes the stopcock, which is fitted to the flask containing the ferrous chloride, &c., and removes the lamp; a slight vacuum is then produced within the flask, and the nitric oxide makes its escape from the liquid into the area of diminished pressure; after a little time the lamp is replaced, and the stopcock is again opened. This process is especially intended for the estimation of nitric acid mixed with organic matter. The author's results prove that the process is very satisfactory in every respect; for its special purpose he regards this method as the best that has yet been proposed.

Reichardt (*Zeitschr. Anal. Chem.*, ix, 24) has proposed to collect the nitric oxide in a vessel containing soda, and thus to do away with the use of mercury. If the hydrogen which is used in the process be very pure, and if the soda solution be freed from air, the results are good, although not quite so rigorously exact as those obtained by the use of the original method.

Wagner (*Dingl. polyt. J.*, 201, 423) decomposes the nitrate by fusion with soda and chromium oxide, receives the nitric oxide in a vessel containing soda-solution and oxygen, and determines the residual alkali. The author's results show that this method is satisfactory, provided no organic matter be present. The process is not, however, so good, or so readily carried out, as that of Schlösing.

β. *The nitric oxide produced is directly measured.* The nitric oxide is produced as in Schlösing's process. The author adopted Tiemann's modification of the process (*Deut. Chem. Ges. Ber.*, vi, 1034), in which, as recommended by Reichardt, the use of mercury is replaced by that of caustic soda. The results were very satisfactory. The method is well adapted to the determination of nitric acid in well-waters. If the substance under examination be a complicated mixture, such as tobacco or other organic bodies, the author gives the preference to the method of Schlösing described under *α*.

B. METHODS DEPENDING ON THE TRANSFORMATION OF THE NITRIC ACID INTO AMMONIA.—The processes of Schulze, Harcourt, &c., &c., have been examined; the author regards this method of determining nitric acid as one of the best, provided that certain conditions be rigorously complied with. His process, in which he claims to have eliminated all sources of error, is as follows:—The apparatus consists of a moderate-sized retort, the beak of which is turned upwards, and is brought into communication with a small flask, which is closed by a caoutchouc cork. An exit-tube from the flask is bent twice at right angles, and communicates with a Peligot's bulb-apparatus, containing a measured quantity of normal sulphuric acid. A somewhat elongated bulb is blown upon the exit-tube from the flask, near the latter. The bulbs containing the acid are connected with an aspirator. A funnel tube, fitted with a stopcock and drawn out to a narrow opening, and curved at its lower extremity, passes through the tubulus to the bottom of the retort. The retort and the flask both rest upon wire gauze. The weighed quantity of nitrate is brought into the retort, finely granulated zinc and iron filings, in the proportion of 2 : 1, as recommended by Harcourt (this *Journal*, xv, 385) are added, and mixed with the nitrate by shaking, about 50 c.c. of caustic potash solution of sp. gr. 1·15 to 1·25 are then allowed to flow into the retort through the funnel tube, and the whole is allowed to remain undisturbed at the ordinary temperature for an hour. After the expiry of that time, distillation is commenced by gradually heating the contents of the retort to boiling, and is continued until from 5 to 10 c.c. of liquid has passed over into the small flask. A tolerably rapid stream of air—freed from ammonia and ammonium salts—is now sucked through the apparatus, without discontinuing the distillation; the small flask is heated, and the operation is continued until but little liquid remains in the flask. The residual acid is determined by titration with $\frac{1}{10}$th normal soda solution.

Special experiments showed that the gravity of the potash solution may vary within the limits given above. If the liquid be heated immediately, the alkaline solution is poured upon the nitrate, the results are unsatisfactory. The more concentrated the potash-solution the greater is the error introduced by omitting the preliminary digestion at the ordinary temperature. The same zinc and iron should not be used more than once. The combination of zinc and iron is quite as good as aluminium, and is much more readily procured. The use of platinised zinc does not give good results.

Alcoholic potash solution has been recommended in order to prevent bumping: by making use of a current of air bumping is avoided, and alcohol need not be used: the current of air also insures the complete carrying over of the ammonia into the titrated acid.

M M. P. M.

Determination of Nitrous Acid and Organic Matter in Potable Waters. By R. HERCHER (*Arch. Pharm.* [3], x, 436—439).—Schönbein's test for nitrous acid is condemned as of little value.

Separation of iodine from an iodide—zinc iodide is the best—is recommended as a good test. The test depending upon oxidation of ferrous sulphate, serves to detect 0·00025 mgm. nitrous acid in 100 c.c. of water.

The amido-benzoic acid test is much less delicate than the preceding.

Of the quantitative tests for nitrous acid, the permanganate is the best, but even this is not very satisfactory.

There is nothing of any importance in the author's remarks upon organic matter in waters. M. M. P. M.

Action of Tartaric Acid on Calcium Carbonate. By B. J. GROSJEAN (*Chem. News*, xxxv, 190).—Both precipitated carbonate and whiting, were digested in 20 parts of boiling water containing 4 pts. of tartaric acid. Neither carbonate was dissolved, even when the acid was doubled and concentrated to a syrup. But addition of water caused solution even in the cold. Thus a weak solution of tartaric acid acts better than a strong solution of *the same weight of acid* on calcium carbonate. If, however, the carbonate is treated with 20 parts of water *saturated* with tartaric acid, solution is brought about by heating, even without dilution. B. J. G.

Determination of Manganese in Spiegeleisen and Ferromanganese. By SERGIUS KERN (*Chem. News*, xxxv, 270).—In order to estimate the manganese in iron alloys, the author some time ago recommended direct ignition of the powdered sample with ammonium chloride. Since then this process has been improved and found by experiment to suit well for technical purposes. 0·5 gram. of the fine powder is intimately mixed with 6 grams of ammonium chloride in a high platinum crucible in which the mass is strongly ignited. By the following reaction the iron is converted into ferric chloride, which partly flies away and partly sublimes on the cover of the crucible:— $6NH_4Cl + Fe_2 = Fe_2Cl_6 + 6NH_3 + 3H_2$. When all the ammonium chloride is decomposed, the cover is removed and the ferric chloride washed off by water. Into the crucible a new quantity of ammonium chloride is put and the mass re-ignited, the operation being repeated till the sublimation of ferric chloride ceases. The residue is dissolved in 25 c.c. of aqua regia and evaporated; the dry mass is mixed with a solution of 10 c.c. of hydrochloric acid in 15 c.c. of water, and the resulting precipitate filtered off. The filtrate is concentrated, poured into a platinum crucible, and dried, the resulting mass being ignited until constant in weight. The remaining brownish-black compound is mangano-manganic oxide, Mn_3O_4, which contains 72·05 per cent. of manganese. D. B.

On the Estimation of Manganese and Phosphorus in Spiegeleisen. By C. Stöckmann (*Zeitschr. Anal. Chem.*, xvi, 172—179).

Manganese.—The process employed for precipitating the iron consisted in almost neutralising the acid solution with sodium carbonate, and then precipitating the hot solution by boiling, after addition of sodium acetate, the manganese remaining in the filtrate. The author finds that the quantity of manganese precipitated with the iron may be sufficiently great to render the results inaccurate, and his experience leads him to insist on the necessity of dissolving the precipitated basic iron acetate in acid, and repeating the precipitation of the iron by sodium acetate: the first and second filtrates being then united for the manganese estimation. The filtrate from a second repetition of the precipitation will still furnish manganese, but in quantity so small as not to materially affect the result. A statement of the analytical results shows quantities of manganese in the second filtrate varying from 1·04 to 0·25 per cent., as much as one-tenth of the total quantity of manganese present being precipitated with the iron, and therefore appearing in the second filtrate. Eggertz has stated that the quantity of manganese carried down in the iron precipitate is insignificant; the author attributes this to the precipitation of the iron in a rather acid solution, which, whilst it tends to hinder co-precipitation of manganese, causes the iron acetate to go down in such a condition as to render filtration extremely difficult. The temperature at the time of precipitation has also much influence on the result; less manganese appears to be precipitated at a high than at a low temperature. This second precipitation of the iron is necessary for its complete separation from manganese, not in analyses of spiegeleisen only, but also in analyses of pig-iron and iron ores containing manganese. The author considers that the different results obtained by different analysts from the same sample of iron may arise from the neglect of the reprecipitation of the iron.

Phosphorus.—The percentage of phosphorus found differed according as nitric acid or aqua regia was used as the solvent, the variation being greater the larger the percentage of phosphorus present, and reaching from 0·007 to 0·037 per cent. in ten analyses, in which the total phosphorus ranged from 0·097 to 0·171 per cent. The solution in nitric acid gave the higher percentage of phosphorus; this had been already rendered probable by the author's own determinations of phosphorus in the same sample of iron, using nitric acid and aqua regia separately as solvents, and also by comparison of his own results when nitric acid had been employed, with those of other analysts who used aqua regia. A careful series of analyses, in some of which pure nitric acid of sp. gr. 1·2 was used, and in others aqua regia of varying, composition, fully confirmed the truth of the above apparent loss of phosphorus during solution of the iron in aqua regia. In a number of determinations of phosphorus in the same sample, the particulars and results of which are given, there was in all cases a smaller percentage shown by aqua regia than by nitric acid solutions. By an experiment, in which the gases evolved during solution in aqua regia were passed through an absorption apparatus, the author proved that phosphorus passed over into the absorption apparatus, and was there readily detected. Hence the author concludes that *aqua regia must be altogether rejected as a solvent for spiegeleisen and other kinds of iron and steel, when phosphorus is to be determined in the solution, because a part of the phosphorus always escapes with the gases, and hence the results obtained would always be too low.*

In the above series of experimental analyses, the percentages of phosphorus were also relatively lower when the precaution was neglected of evaporating the acid solution to dryness and igniting the residue in order to destroy organic substances: these organic substances seem to have the power of preventing the entire precipitation of phosphoric acid by the ammonium-molybdate solution.

On account of the great importance of phosphorus determinations in iron and steel, the method employed by the author is fully described. It yields constant and apparently trustworthy results, and is carried out as follows:—5 grams of powdered spiegeleisen are dissolved in a beaker of 800—1000 c.c. capacity covered by a watch-glass, by adding gradually 60 c.c. of pure nitric acid of sp. gr. 1·2: as soon as the frothing is over the liquid is heated to boiling upon a sand-bath until the substance is entirely dissolved; this takes place in ten minutes at most. The solution is removed to a porcelain crucible of 250 c.c. capacity, and evaporated to dryness on the sand-bath; the residue is then ignited until the carbon, or at least the organic substances in it, are entirely destroyed, loss by spirting being carefully guarded against during the evaporation and ignition, by covering the crucible when necessary. The cool residue is then dissolved by heating it with hydrochloric acid, the solution is filtered into a beaker, and the free acid removed by boiling almost to dryness and neutralising the remainder with ammonia. Nitric acid is added and heat applied until a perfectly clear solution is obtained, and to this, when cool, 50—60 c.c. of the ammonium-molybdate solution are added: the precipitation is complete after 12—24 hours' standing at a temperature of 30—40° C. After filtration the precipitate is washed with a mixture of 100 molybdate-solution, 20 nitric acid, and 80 water: it is then dissolved in dilute ammonia; the solution is nearly neutralised with nitric acid; and, when it is cool, magnesium chloride solution and ammonia are added until the volume of the liquid is 100—110 c.c. The precipitate thus obtained is ignited and weighed. F. C.

New Method of estimating Ferrous Oxide in Silicates which are insoluble in the ordinary Mineral Acids. By A. R. LEEDS (*Zeitschr. Anal. Chem.*, xvi, 323—326).—What the author claims to be new in this method is the preparation of hydrofluoric acid used for dissolving the silicate. The finely powdered mineral treated with a suitable quantity of dilute sulphuric acid is, in the first place, surrounded by an atmosphere of carbonic acid gas and then exposed to the action of hydrofluoric acid. The following are the advantages of this method :—(1.) It renders a previous preparation of pure concentrated hydrofluoric acid unnecessary. (2.) The quantity of acid required for solution is very small, amounting only to a few cubic centimeters, and no more acid need be prepared than the quantity necessary for each analysis. (3.) The mixing of mineral and solvent does not take place in the air, which in fact is completely excluded: it is therefore not necessary to transfer the mixture afterwards to a non-oxidising atmosphere. The author strongly recommends Cooke's method of estimating ferrous oxide by dissolving in hydrofluoric acid and titrating with permanganate of potassium. The finely pulverised mineral is in the first place mixed with concentrated hydrofluoric acid and sulphuric acid, then dissolved by warming the mixture on a water-bath, which is covered with a funnel through which a continuous stream of carbonic acid gas is passed. D. B.

Determination of Copper in "Ore Reducer" Slag. By T. C. CLOUD (*Chem. News*, xxxv, 259).—A sample of "ore reducer" slag was ground down in an agate mortar to an impalpable powder, and 2 grams of the powder digested with nitro-hydrochloric acid for 24 hours in a covered beaker. At the end of this time the cover was removed, and after this cover and the sides of the beaker had been washed with water, sulphuric acid was added, and the contents of the beaker were evaporated until the fumes of this acid began to be given off. Cool water was added, and the copper determined by electro-deposition on a weighed platinum cylinder forming the cathode of a two-cell Daniell's battery. When all the copper had been thus deposited from the solution, the platinum cylinder was removed, washed successively with boiling water and with alcohol, dried at 100°, and re-weighed. Copper obtained 0·25 p. c. Another portion of the sample, treated as above described, but with the addition of a small quantity of concentrated sulphuric acid, previous to the nitro-hydrochloric acid, gave 0·35 p. c. of copper. It was evident, from the appearance of the contents of the beaker, that decomposition had proceeded farther than in the first instance, but a large quantity of dark-coloured silicate yet remained. After the copper had been removed from the solution, the insoluble residue was dried, and again treated with acid as before for 24 hours. The solution again yielded copper. In the next experiment, the slag was treated by the fusion-method with bisulphate of potash, the sample after treatment yielding 0·59 p. c. of copper. The slag was finally fused with 4 parts of the mixed carbonates of potash and soda, and one-fourth part of nitrate of potash. After determining the copper as above described, 0·64 p. c. was obtained. The second method is the more trustworthy. D. B.

Method of Estimating Copper and Sulphur in Cupreous Iron Pyrites and in the Burnt Ore before and after Lixiviation. By R. FRESENIUS (*Zeitschr. Anal. Chem.*, xvi, 335—341).—1. *Drying of the substances:* a. Estimation of moisture. The samples for analysis must be kept in well-stoppered bottles. About 25 grams of pyrites or 10 grams of burnt ore are heated on a water-bath in a large clock-glass (6—7 cm. diameter), until constant in weight. Four hours' heating will be found long enough for any sample. When the sample is heated to 120°, it alters slightly, but the variation is so slight that it suffices to heat the substance at 100°. The following figures show what differences are obtained when the substance is dried at 100° and at 120°:—

	Substance used.	Loss of water at 100°.	Loss of water at 120°.
Pyrites..........	25·1825	0·136	0·156
Burnt ore........	10·5920	2·728	3·049
Burnt or lixiviated	10·3230	15·601	15·615

b. *Preparing the substance to be analysed.*—A large quantity of the sample for analysis is broken up into small fragments and the whole sifted through a coarse iron sieve. After mixing the sifted mass very carefully, about one-fourth of it is powdered and passed through a finer sieve. About 15 grams of the intimately mixed powder are put into an agate mortar, and ground up very finely. The powdered sample is then kept in small sample-tubes, which are well-corked. It is best to divide the sample into two lots, and to use the contents of the largest tube for determining the copper, and the smaller portion for estimating the sulphur. By weighing the tared tubes before and after part of the contents have been taken out, the weight of the quantity used for analysis is obtained.

2. *Determination of Copper.* a. Dissolving the substances.

α-Pyrites.—Since the latter contain about 3 p. c. of copper, 5 grams yield about 0·190 gram of sulphide of copper. A difference of 0·001 gram in the weight of sulphide corresponds with a difference of 0·016 in the percentage of copper, which may be overlooked. 5 grams of pyrites are, therefore, warmed with 6—7 c.c. of hydrochloric acid of 1·17 spec. grav., and treated gradually with concentrated nitric acid of 1·37 spec. grav. until no further reaction is perceived. The mixture is then digested at a moderate heat for several hours. The solution is best made in a flask. At the end of the operation, the contents of the flask are poured into a porcelain basin and the flask washed out with hydrochloric acid of 1·12 spec. grav., using 20 c.c. for washing. The liquid is then evaporated nearly to dryness, treated with 20 c.c. of hydrochloric acid of 1·12 spec. grav., warmed, diluted with water, and filtered into a flask holding about 500 c.c. Should any residue be left in the flask used for dissolving, it is to be washed on the filter. The filter and contents are then dried, incinerated, and the residue treated in a porcelain crucible with 1 c.c. of aqua regia (consisting of 3 parts HCl, sp. gr. 1·17, and 1 part HNO_3, sp. gr. 1·37), evaporated to dryness, warmed with 5 c.c. of hydrochloric acid of 1·12 sp. gr., diluted, and filtered. The filtrate is added to the main solution. The insoluble grey residue is now free from copper.

β. Burnt-ore (lixiviated or unlixiviated).—About 3·5—4 grams of the ore are warmed with 24 c.c. of hydrochloric acid of 1·17 sp. gr., and 6 c.c. of nitric acid of 1·37 sp. gr. The solution is diluted, the black residue filtered off and washed, the filter is then incinerated, the residue treated in the crucible with 1 c.c. of hydrochloric acid of 1·17 sp. gr. and a few drops of nitric acid, evaporated, warmed with 2 c.c. of hydrochloric acid of 1·12 sp. gr., and filtered, adding the filtrate to the main solution, which is finally made up to 400 c.c.

b. *Separation and Estimation of the Weight of Copper.*—The solutions of pyrites or of burnt ore are precipitated with sulphuretted hydrogen at 70°. The precipitate is filtered, washed, and dried. It is placed on a clock glass, and after incinerating the paper, the precipitate and ash are put in a porcelain crucible and heated to redness. The residue is then warmed with 5 c.c. of nitric acid of 1·2 sp. gr., diluted, filtered into a porcelain dish, and washed. The filter is incinerated, the residue again warmed with 2 c.c. of nitric acid, diluted, filtered, washed, and the filtrate mixed with the main solution. The solution containing nitrate of copper and nitrate of lead, is treated with 12 c.c. of dilute sulphuric acid (1 sulphuric anhydride, 5 water), evaporated on a water-bath till all nitric acid is expelled, the residue treated with water, and the sulphate of lead filtered off and washed with acid water. The filtrate is treated with sulphuretted hydrogen at 70°, and the precipitated sulphide of copper washed, dried, mixed with sulphur, and heated in a stream of hydrogen.

3. *Estimation of Sulphur.*—a. In pyrites.—A mixture of 2 parts of dry sodium carbonate and 1 part of potassium nitrate is required. Both reagents must be free from sulphuric acid. About 0·5 gram. of the finely-powdered sample dried at 100°, is mixed with 10 parts of the above mixture, and put in a platinum crucible. The top of the crucible is covered with a thin layer of the mixture and the whole heated over a Berzelius' spirit lamp, until the mass melts. The latter is then cooled, warmed with water, and carbonic acid gas introduced, in order to precipitate the small quantity of lead oxide which has gone over into the alkaline solution. The solution is filtered, the residue boiled with a solution of pure sodium carbonate, filtered, and washed with boiling water (to which sodium carbonate has been added), until the washings are free from sulphuric acid. The filtrate and washings are acidified with pure hydrochloric acid, warmed to expel the carbonic acid, and freed from nitric acid by repeated evaporation with pure hydrochloric acid. The final residue is moistened with 2 c.c. of dilute hydrochloric acid, treated with water, heated, filtered, and the hot solution precipitated with a moderate excess of chloride of barium. After filtering and washing, the precipitate is dried, incinerated, ignited, and weighed. The barium sulphate obtained is often not quite pure; it is, therefore, best to treat the ignited residue with hydrochloric acid and reignite.

b. *Determination of Sulphur* in the lixiviated and not lixiviated residues. A mixture of 4 parts anhydrous sodium carbonate and 1 part potassium nitrate is required. Both reagents must be perfectly pure, especially free from sulphuric acid. About 1 gram of the powder, dried at 100°, is mixed in a platinum crucible, with 5 parts of the above mixture, and treated exactly in the same manner as under 3 a.

D. B.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXVII.—*On the Oxidation of Ditolyl.*

By Thos. Carnelley, D.Sc. (Lond.), Demonstrator in the Chemical Laboratory of the Owens College.

Last year I published a paper (*Chem. Soc. Jour.* [2], xiv, 13) on the new hydrocarbon, tolyl-phenyl, in the production of which a quantity of both liquid and solid ditolyl was obtained as bye-product. Almost six months before my paper appeared in the *Journal*, *i.e.*, in the autumn of 1875, I commenced a research on the oxidation of these two ditolyls, and obtained two new acids. I discontinued, however, for some time to work at this subject, as I hoped to obtain a much larger quantity of ditolyl, and intended not to proceed till I had done so. Rather more than a month ago I happened to see a paper by Doebner, on the oxidation of this hydrocarbon, in the *Journal of the Berlin Chemical Society*, ix, 271, in which he describes the oxidation of solid ditolyl (m. p. 121°) to diphenyldicarbonic acid. At the end of his memoir he said he was continuing his research, but does not give any further results. Owing to an oversight, I was unfortunate not to see his paper, which appeared in February, 1876, till a few weeks ago. It is evident, however, from what has been said, that I had succeeded in obtaining two of the products of the oxidation of ditolyl previous to the publication of Doebner's paper, both of them being entirely new acids. As I have not seen any further communication by Doebner on this same subject, I have hastened during the last month to complete my own investigation with what material I had, and without waiting till I had more at command. The following paper contains the results I have obtained:—

According to Zincke (*Deut. Chem. Ges. Ber.*, iv, 396), two isomeric ditolyls are obtained by the action of sodium on the (1 : 4) monobromotoluene—

(1.) Solid, m. p. 121°, b. p. 283—288°.
(2.) Liquid, b. p. 283—288°.

The ditolyl got by Fittig from crude monobromotoluene (*i.e.*, a mixture of the (1 : 2) and (1 : 4) isomerides) boiled at 272°, while that prepared from monochlorotoluene boiled at 273—278°. Only a small quantity of solid ditolyl could be produced by Zincke from crude brom- or chlorotoluene.

The crude ditolyl obtained in the preparation of tolyl-phenyl was fractionated, when from the portions boiling at 270—290° crystals of solid ditolyl separated out, and thees, after pouring off the liquid, were recrystallised twice from hot alcohol. The pure solid ditolyl thus obtained melted at 119—120°, and crystallised in hard, white, glistening plates.

The fractions of liquid ditolyl, after the separation of the solid modification, were placed in a freezing mixture, but no further separation of crystals occurred. They were then divided into two portions (1) b. p. 270—280°, (2) b. p. 280—290°. There was nearly an equal quantity of each, the former being rather in excess.

The solid ditolyl and the two fractions of the liquid were then each oxidised separately.

I. OXIDATION OF SOLID DITOLYL, M. P. 121°.

(*a.*) *Incomplete Oxidation.*—1·147 grams of the hydrocarbon were placed in a flask and dissolved in glacial acetic acid; 2·294 grams of crystallised chromic acid were then added gradually, with frequent shaking. After the somewhat violent action had ceased, the liquid was boiled for about an hour, cooled, and poured into a large quantity of cold water, allowed to settle, and then filtered. The precipitate of acid and unchanged hydrocarbon, after washing, was treated with ammonia and filtered, and the acid thrown down from the filtrate by hydrochloric acid as a white flocculent precipitate; it was filtered off and washed with cold water. The moist acid thus obtained was insoluble in cold, but easily soluble in hot water and in alcohol; after drying, however, it was only difficultly soluble in hot water, and even in boiling alcohol; in ether it dissolved more readily. It forms a very difficultly crystallisable ammonium salt. It melted, with blackening, at 245° C.

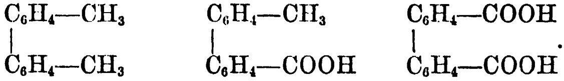
It was boiled for some time with alcohol and filtered, and the residue of acid dried. It then melted, with blackening, at 243—244°, *i.e.*, nearly the same as before, from which it was concluded that it was pure. The silver salt was prepared from the ammonium salt by double precipitation with silver nitrate, as a thick, curdy, white precipitate, which was soluble in a moderate quantity of boiling water, and on cooling reprecipitated as a white amorphous powder. The dried salt was analysed.

(1.) ·204 gram salt gave ·0685 gram Ag = 33·58 per cent. Ag.
(2.) ·097 „ „ ·0335 „ = 34·53 „

Calculated for $C_{12}H_8\left\{\begin{matrix}CH_3\\COOAg\end{matrix}\right.$	Found. (1)	(2)	Mean.
Per cent. Ag = ... 33·85	33·58	34·53	34·05

This proves that the first product of oxidation of solid ditolyl is tolyl-phenylcarbonic acid, $CH_3—C_6H_4—C_6H_4—COOH$.

(*b.*) *Complete Oxidation.*—As all the solid ditolyl I had at my disposal had been used for the previous experiments, it was not possible to investigate the result of the complete oxidation of this hydrocarbon, but this deficiency is supplied by the results obtained by Doebner in the paper already referred to. He found that solid ditolyl, m. p. 121°, on oxidation with excess of chromic acid, gave an acid which was insoluble in all solvents, and neither sublimed nor melted, and formed very difficultly soluble salts, and on heating with excess of lime gave diphenyl. These properties, and the analysis of the ether (m. p. 112°), proved it to be diphenyldicarbonic acid, and identical with the acid obtained from dicyanodiphenyl. The oxidation of solid diphenyl is therefore represented thus—



$$\begin{matrix}C_6H_4—CH_3\\|\\C_6H_4—CH_3\end{matrix}\qquad\begin{matrix}C_6H_4—CH_3\\|\\C_6H_4—COOH\end{matrix}\qquad\begin{matrix}C_6H_4—COOH\\|\\C_6H_4—COOH\end{matrix}.$$

II. OXIDATION OF LIQUID DITOLYL, B. P. 280—290°.

(*a.*) *Incomplete Oxidation.*—2·15 grams of the hydrocarbon were dissolved in glacial acetic acid, and 6·14 grams of chromic acid added gradually, and treated as above described. As the acid thus obtained was not quite colourless, it was dissolved in ammonia and boiled with animal charcoal, filtered, and reprecipitated with hydrochloric acid; m. p. = 176°. The melting point of another preparation was found to be 173—177°. The acid was insoluble in water and in cold alcohol, but soluble in hot; it formed a soluble ammonium salt, and on precipitation of the latter with barium chloride, it gave a white curdy barium salt, which was but very slightly soluble in water. The silver salt was obtained by double precipitation with silver nitrate as a white flocculent precipitate. Two analyses of this last salt yielded the following results:—

(1.) ·0664 gram of the salt gave ·0228 gram Ag = 34·33 p. c. Ag.
(2.) ·0994 „ „ ·0340 „ = 34·20 „

Calculated for $C_{12}H_8\left\{\begin{matrix}CH_3\\COOAg\end{matrix}\right.$	Found. (1)	(2)	Mean.
Per cent. of Ag = ... 33·85	34·33	34·20	34·26

These results show that when the liquid ditolyl (b. p. 280—290°) is oxidised with a deficit of chromic acid, the product is an acid having the composition $CH_3—C_6H_4—C_6H_4—COOH$, being isomeric with that obtained by the incomplete oxidation of the solid ditolyl.

(*b.*) *Complete Oxidation.*—2·2 grams of the hydrocarbon were oxidised in the manner already described, by 24·0 grams (*i.e.* an excess) of chromic acid.

The acid resulting from this oxidation was a white powder insoluble in all the usual solvents; it did not melt, but sublimed without decomposition, in the form of white crystalline grains. By double decomposition of the ammonium salt, a white insoluble silver salt was produced, which on analysis gave 55·65 per cent. of silver, while the silver salt of terephthalic acid requires 56·84 per cent.

The above proves, then, that on complete oxidation, liquid ditolyl, b. p. 280—290°, gives terephthalic acid.

(*c.*) *Intermediate Oxidation.*—In order to see whether an intermediate acid could be produced of the composition

$$COOH.C_6H_4.C_6H_4.COOH,$$

and isomeric with the diphenyldicarbonic acid obtained by Doebner from solid ditolyl, 2·2 grams of the hydrocarbon were dissolved in glacial acetic acid and oxidised with 15·5 grams of chromic acid. The liquid on cooling was poured into water, and the precipitate of acid filtered off and washed with water. On treating with ammonia it left a rather large residue insoluble even in the boiling liquid. This residue was filtered off and washed; as it was not oily, and was insoluble in alcohol, it could not be unchanged hydrocarbon.

The residue and filtrate were treated separately as follows:—

Residue was warmed with alcohol to dissolve out any unchanged hydrocarbon, and filtered. The alcoholic filtrate on evaporation gave a very small quantity of an oily residue, which was too small to work with. The residue insoluble in alcohol was washed with water and treated with dilute hydrochloric acid, to convert the supposed insoluble ammonium salt into acid; a yellowish-white residue was left, but was too small to do anything with.

The filtrate, treated with hydrochloric acid, gave a white flocculent precipitate, which, after washing and drying, blackened without melting below 270°, and sublimed readily on heating. The acid thus obtained was boiled with a small quantity of alcohol, and filtered, the object being to separate any $C_{12}H_8\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.$, that would probably be more soluble than the dicarbonic acid $C_{12}H_8\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$, if the latter were present.

The *residue* was dried. It sublimed, without melting, in small needles, and blackened at about 230°. The silver salt was prepared in the ordinary way as a white insoluble amorphous precipitate, which yielded, on analysis, the following:—

·0835 gram salt gave ·0394 gram Ag = 47·18 per cent. Ag.

Calculated for $C_{12}H_8\left\{\begin{matrix}COOAg\\COOAg\end{matrix}\right.$ .... = 47·37.

The alcoholic filtrate was evaporated to dryness to drive off the alcohol, the residue dissolved in ammonia, and the solution precipitated by hydrochloric acid. The white flocculent precipitate, after washing and drying, blackened at 230°, and did not melt when strongly heated, but readily sublimed. It was difficultly soluble in alcohol or ether, whether hot or cold. The silver salt was prepared and analysed.

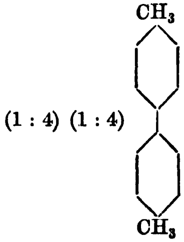
·1142 gram salt gave ·0531 gram Ag = 46·50 per cent. Ag. The acid would, therefore, appear to be identical with that in the above residue, except that it contained probably a very small quantity of $C_{12}H_8\left\{\begin{matrix}COOH\\CH_3\end{matrix}\right.$.

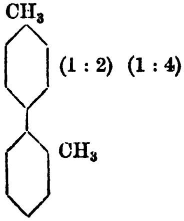
The liquid ditolyl, therefore, on oxidation as shown by the above results, gives first $C_{12}H_8\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.$, then $C_{12}H_8\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$, and finally terephthalic acid $C_6H_4\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$.

III. Oxidation of Liquid Ditolyl, b. p. 270—280°.

This fraction gave exactly the same products on oxidation as that which boiled at 280—290°, proving them to be practically identical.

The above experiments show, therefore, that when sodium acts on parabromo-toluene, two isomeric ditolyls are produced, one of them being, as will be pointed out below, the di-para, and the other the ortho-para-ditolyl. Thus:





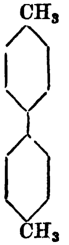
The formation of the second of these bodies is probably due to the fact, that in the preparation of ditolyl by different chemists, the solid

(1·4) monobromo-toluene employed was not perfectly pure, but contained a small quantity of the isomeric liquid (1 : 2), monobrom-compound.

The ditolyl (b. p. 272°) which Fittig obtained by the action of sodium on crude monobromo-toluene (*i.e.*, a mixture of the para- and ortho-compounds), was probably a mixture of the above two ditolyls, the liquid modification, as pointed out by Zincke, being greatly in excess, the solid in fact being produced in only very small quantity. If we make no allowance for a difference in the thermometers, this tends to show that of the two the liquid (1 : 4) (1 : 2) ditolyl has rather the lower boiling point, notwithstanding that Zincke found the two hydrocarbons obtained from the nearly pure parabromotoluene to boil at almost the same point, viz., 283—288°, and this is what theory would lead us to expect, for para compounds, as a rule, boil higher than ortho, and therefore probably also higher than ortho-para.

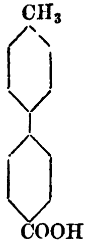
The following formulæ show the manner in which the atoms are arranged in the different compounds which have been mentioned in the preceding pages, together with three others, viz., VIII, IX, and X :—

I.



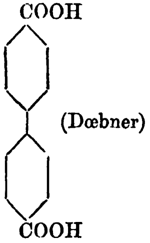
Diparaditolyl (1 : 4) (1 : 4) solid.
M. p. = 121°; b. p. = 283—288°.

II.



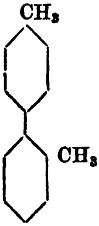
Dipara-tolyl-phenyl carbonic acid (or tolyl benzoic (1 : 4) (1 : 4).
M. p. = 244°.

III.



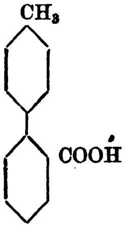
Dipara-diphenyl-dicarbonic acid (or dibenzoic) (1 : 4) (1 : 4).
Does not melt.

IV.



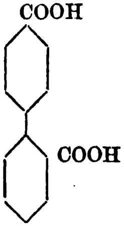
Ortho-para-ditolyl (1 : 2) (1 : 4) liquid.
B. p. = 283—288°.

V.



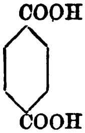
Ortho-para-tolyl-phenyl carbonic acid (1 : 2) (1 : 4).
M. p. = 176°.

VI.



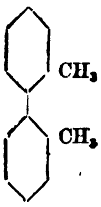
Ortho-para-diphenyl dicarbonic acid (1 : 2) (1 : 4).
Does not melt.

VII.



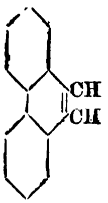
Terephthalic acid (1 : 4).
Does not melt.

VIII.



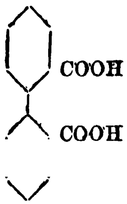
Wanting
(1 : 2) (1 : 2).

IX.



Phenanthrene
(1 : 2) (1 : 2).
M. p. = 100°;
B. p. = 340°.

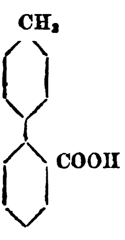
X.



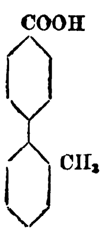
Diortho-diphenyl-dicarbonic
acid (Fittig and Ostermayer's
diphenic acid) (1 : 2) (1 : 2).
M. p. = 226°; readily soluble
in alcohol and ether.

Since the purest para monobromo-toluene gives with sodium the solid ditolyl in by far the greater quantity, it follows that this latter hydrocarbon has the constitution represented by I, and as the acids II and III are derived from it by oxidation, they will also be dipara-compounds. Further, since the ordinary diderivatives of diphenyl are dipara compounds, it is probable that Doebner's dicyanodiphenyl derived from the disulphonic acid is also a dipara-compound; and as it gives the acid III on treatment with alcoholic potash, it is likewise probable that this acid has the constitution given to it above, and is therefore a dipara-compound, as is also proved by its formation from solid ditolyl.

The production of liquid ditolyl from a mixture of ortho- and para-bromo-toluene, and the fact that solid ditolyl is a dipara-compound, show that the former hydrocarbon must be either a diortho- or an ortho-para-compound; while the formation of terephthalic acid, as the final product of oxidation, proves it to be the latter, as shown in IV, and consequently that the two acids V and VI are likewise ortho-para. The only point which remains to be settled is, whether the acid V is—



or



I think, however, there is no doubt that it is the former, for the ortho-methyl would undergo oxidation the more easily of the two, and would therefore be first oxidised.

The relation of phenanthrene and its derivative, diphenic acid, to the preceding compounds is shown in IX and X, the hydrocarbon

VIII being still unknown. A secondary result of the above experiments is, that they go to confirm in a great measure the generally received constitution of phenanthrene (viz., as a di-ortho-compound IX); for inasmuch as it yields on oxidation diphenic acid, it cannot be either a di-para- or an ortho-para compound, for, if so, it would yield, not diphenic acid, but one of the acids III or IV. It must, therefore, be a di-ortho, a di-meta, a meta-para, or a meta-ortho compound. That it cannot be a di-para-compound is shown by the fact that diphenic acid may be converted into phenyl-benzoic acid, $C_6H_4\left\{\begin{matrix}COOH\\C_6H_5\end{matrix}\right.$, which latter is not a para-compound, being isomeric with the para-phenyl-benzoic acid obtained from (1:4) tolylphenyl.

With respect to the four remaining possible constitutions for phenanthrene, its whole chemical character shows that it stands in the same relation to naphthalene as the latter to benzene (Schorlemmer), and it is therefore almost certainly a di-ortho compound. The fact that diphenic acid melts indicates also that it is probably di-ortho.

I intend, if possible, to prepare di-ortho-ditolyl from orthobromotoluene, and to investigate its products of oxidation, one of which should be diphenic acid, if phenanthrone be really a di-ortho compound.

XXVIII. *On some Hydrocarbons obtained from the Homologues of Cinnamic Acid; and on Anethol and its Homologues.*

By W. H. PERKIN, F.R.S.

As the new acids I have lately obtained from the aromatic aldehydes (p. 388 of last volume) are homologues of cinnamic acid, it was of interest to see if hydrocarbons similar to cinnamene could be prepared from them. This had been shown to be the case in one instance, namely, in that of cumenyl-acrylic acid, iso-propyl-vinyl-benzene being obtained. I have now further examined this hydrocarbon, and obtained several new ones.

The acids I have employed were cumenyl-acrylic, -crotonic, and -angelic, and phenyl-crotonic and -angelic, of which it was necessary to prepare considerable quantities. I find a much lower temperature than that I previously used for their production answer quite as well, if not better, about 140—150° C. being sufficient, the product being kept at this point for about twenty-four hours. The amount of anhydride I also considerably reduced, using only about the same weight as that of the aldehyde employed; by working in this manner less carbonic anhydride is formed, and the yield of the acids increased.

At the commencement of this investigation the preparation of the hydrocarbons from the above acids was effected by decomposing them by heat, in the same manner as cinnamene is prepared from cinnamic acid. This process worked moderately well with some acids, but not so well with others; however, whilst so engaged, my attention was called to a paper entitled "Communications from the Chemical Institute of the University of Strasburg," by R. Fittig (*Deut. Chem. Ges. Ber.*, 1877, p. 513). In this there is an account of the additive-products of cinnamic acid, by F. Binder, who shows that hydrobromo- or hydriodocinnamic acid, when treated with bases, not only loses hydrobromic or hydriodic acids, but also carbonic anhydride, chemically pure cinnamene being produced in considerable quantities. I therefore naturally endeavoured to produce additive-products of the acids I was working with, in order to see if they also would decompose when treated with bases, and yield the corresponding hydrocarbons. In all cases I succeeded in obtaining them, several being prepared in a sufficiently pure state for analysis.

I have worked only with the hydrobromo additive-products. These were obtained by simply leaving the finely divided acid in contact with fuming hydrobromic acid, sp. gr. 174, for several days, just as Binder prepared hydrobromocinnamic acid. I also tried a modification of the process, using glacial acetic acid saturated with hydrobromic acid, in place of the aqueous solution, the object being to get the acid to be acted upon in solution. This answers very well, and on exposing the mixture to the air after the action is completed, the new hydrobromo-acid generally separates out in crystalline crusts. The following is an account of these products:—

I. *Hydrobromocumenylacrylic Acid*, $C_{12}H_{15}BrO_2$.—This acid forms brilliant crystals on the evaporation of its ethereal solution. It is very soluble in ether and alcohol. It melts at 85—87° C., and when further heated decomposes with separation of hydrobromic acid. It gave the following numbers on analysis:—

·2387 of substance gave—
·4661 of CO_2, and
·1227 of H_2O.

	Theory for $C_{12}H_{15}BrO_2$.	Experiment.
Carbon	53·13	53·24
Hydrogen	5·53	5·69

This acid when boiled with water, fuses to an oil, and then becomes pasty, splitting up principally into hydrobromic and cumenylacrylic acids.

Hydrobromocumenylcrotonic acid, $C_{13}H_{17}BrO_2$, crystallises in flat, oblique prisms. It melts at 148—150°, with partial decomposition, and if more strongly heated, hydrobromic acid is given off in abundance. In ether it is extremely soluble, and moderately so in alcohol, benzene, and glacial acetic acid. Petroleum spirit dissolves it with difficulty. It gave the following numbers on analysis:—

·2859 of substance gave—
·5726 of CO_2, and
·1560 of H_2O.

	Theory for $C_{13}H_{17}BrO_2$.	Experiment.
Carbon	54·73	54·62
Hydrogen	5·96	6·05

Hydrobromocumenylangelic acid, $C_{14}H_{19}BrO_2$.—Like the preceding acids, this substance decomposes when heated, with separation of hydrobromic acid. It crystallises in flat prisms, ether dissolves it freely, and it is moderately soluble in alcohol. On analysis it gave the following numbers:—

·2187 of substance gave—
·4438 of CO_2, and
·1232 of H_2O.

	Theory for $C_{14}H_{19}BrO_2$.	Experiment.
Carbon	56·18	55·32
Hydrogen	6·35	6·25

The products obtained by treating phenylcrotonic and phenylangelic acids with hydrobromic acid have not as yet been analysed, but from their properties and products of decomposition there can be no doubt that they are the hydrobromo-acids homologous with hydrobromocinnamic acid.

All the hydrobromo-acids just described decompose when treated with a cold solution of sodium carbonate or potassium hydrate, in an analogous manner to hydrobromocinnamic acid, hydrocarbons being produced. In preparing these, the acids were stirred for some time with a cold solution of sodium carbonate, using an excess. The creamy mixture was then warmed, to facilitate the formation of a layer of the hydrocarbon on the surface; this was collected, distilled with the vapour of water, and then dried.

The alkaline solution from this reaction always contained organic acids, but usually in small quantities, and not sufficient for investigation.

Isopropylvinylbenzene.

This hydrocarbon has been already described to a small extent, and its analysis given in my previous paper. Further preparations of it have been again made, both by the distillation of the acid, and from hydrobromocumenylacrylic acid, by the action of sodium carbonate upon it. The products obtained by these two products were identical.

The formation of this hydrocarbon by these processes may be represented thus:—

I. $C_6H_4(C_3H_7).CH{=}CH.COOH = C_6H_4(C_3H_7).CH{=}CH_2 + CO_2.$
Cumenylacrylic acid. Isopropylvinylbenzene.

II. $C_6H_4(C_3H_7).CH_2.CHBr.COOH = C_6H_4(C_3H_7).CH{=}CH_2 +$
Hydrobromocumenylacrylic acid. Isopropylvinylbenzene.

$HBr + CO_2.$

Isopropylvinylbenzene boils at 203—204°, a considerable quantity polymerising during the distillation, and being left behind. Its sp. gr. at 15° is ·8902. If heated for a few hours to 150° it solidifies to a transparent glassy mass. This change also takes place at the ordinary temperature, and in the presence of daylight, in the course of a month or two. The transformation of this hydrocarbon into the solid product—which is undoubtedly analogous to metacinnamene—is more rapid than that of cinnamene itself.

This polymerised product is insoluble in alcohol, but dissolves readily in benzene, and is left on the evaporation of its solution in this solvent as a hard, brittle, transparent substance. When strongly heated it volatilises, and condenses as an oil, which has all the properties of isopropylvinylbenzene.

The odour of isopropylvinylbenzene is somewhat similar to the hydride of cumyl but more fragrant.

A solution of chromic acid is almost without action on this hydrocarbon unless heat be applied. Iodine dissolves in it to some extent, and when heated with it the mixture rapidly changes into a solid tenacious substance. With fuming nitric acid this hydrocarbon acts with almost explosive violence, and on the addition of water, a sticky yellow product separates out.

Dibromide of Isopropylvinylbenzene, $C_{11}H_{14}Br_2$.—When shaken with bromine and water, isopropylvinylbenzene reacts with energy, producing a solid brominated derivative. On washing this with dilute aqueous potash to remove free bromine, and then crystallising it from alcohol, it is obtained in beautiful brilliant, colourless needles. On analysis the following numbers were obtained:—

·2462 of substance gave
·3901 of CO_2, and
·1045 of H_2O.

	Theory for $C_{11}H_{14}Br_2$.	Experiment.
Carbon	43·13	43·17
Hydrogen	4·57	4·71

This substance melts at 71°. It is very soluble in hot, but only moderately so in cold alcohol.

Heated with an alcoholic solution of potassium hydrate, it rapidly decomposes with separation of potassium bromide, and on adding water to the product, a heavy brominated oil separates, probably $C_{11}H_{13}Br$. This oil, when heated to about 150° for several hours, becomes brown and viscid; hydrobromic acid is also given off.

Isopropylallylbenzene.

The preparation of this hydrocarbon by the action of heat on cumenylcrotonic acid is not very satisfactory, but if the hydrobromocumenylcrotonic acid be employed, on treatment with sodium carbonate a very good yield is obtained. A specimen distilled from sodium gave the following numbers on analysis:—

I. ·2455 of substance gave
·8093 of CO_2, and
·2226 of H_2O.
II. ·2072 of substance gave
·6845 of CO_2, and
·1894 of H_2O.

	Theory for $C_{12}H_{16}$.	Experiment.	
		I.	II.
Carbon	90	89·89	90·09
Hydrogen......	10	10·02	10·10

The formation of this hydrocarbon may be represented thus:—

$$\underset{\text{Cumenylcrotonic acid.}}{C_6H_4(C_3H_7).CH{=}CH.CH_2.COOH} = \underset{\text{Isopropylallylbenzene.}}{C_6H_4(C_3H_7).CH{=}CH.CH_3} + CO_2$$

$$\underset{\text{Hydrobromocumenylcrotonic acid.}}{C_6H_4(C_3H_7).CH_2.CHBr.CH_3.COOH} = C_6H_4(C_3H_7).CH{=}CH.CH_3 + HBr + CO_2.$$

Isopropyl-allyl-benzene boils at 229—230°; its sp. gr. at 15° is ·8900. When cooled to − 15° it does not solidify. Heated for sixty hours to 160—200°, it does not appear to undergo any change.

It dissolves only to a small extent in ordinary concentrated sulphuric acid even when heated, but is apparently polymerised, for on adding water to dilute the acid the oil, which forms a layer on the surface, becomes quite thick on cooling.

Dibromide of Isopropylallylbenzene, $C_{12}H_{16}Br_2$.—Bromine water is rapidly decolorised when shaken with isopropylallylbenzene, and when added until its colour no longer disappears, a heavy oily product is obtained; this, after being washed with aqueous potassium hydrate and allowed to stand, gradually solidifies to a crystalline mass. On pressing this very strongly to remove a brominated oily impurity, it is left as a dry white wax-like cake. It is then further purified by crystallisation from alcohol. On analysis the following numbers were obtained:—

·2430 of substance gave
·4008 of CO_2, and
·1102 of H_2O.

	Theory for $C_{12}H_{16}Br_2$.	Experiment.
Carbon	45·0	44·97
Hydrogen	5·0	5·03

The dibromide of isopropylallylbenzene melts at 59° to a colourless oil, which crystallises beautifully on cooling. It is easily soluble in boiling alcohol, and crystallises from it on cooling in thin plates. It is very soluble in ether and petroleum spirit.

When heated with an alcoholic solution of potassium hydrate it rapidly decomposes, potassium bromide and a heavy brominated oil being produced.

Isopropylbutenylbenzene.

This hydrocarbon is a colourless oil, boiling at 242—243°. Its odour is somewhat like the hydride of cumyl, but more fruity and less powerful. At 15° its sp. gr. is ·8875. When heated to 160—200° for sixty hours it did not thicken or appear in any way to change. It gave the following numbers on analysis:—

I. ·2206 of substance gave
·7216 of CO_2, and
·2023 of H_2O.
II. ·1929 of substance gave
·6342 of CO_2, and
·1800 of H_2O.

	Theory for $C_{13}H_{18}$.	Experiment. I.	Experiment. II.
Carbon	89·65	89·21	89·66
Hydrogen..	10·34	10·18	10·36

The formation of this substance is analogous to the preceding. Its constitution may be written thus:—

$$C_{13}H_{18} = C_6H_4(C_3H_7).CH{=}CH.CH_2.CH_3.$$

Isopropylbutenylbenzene resinifies if kept in contact with the air. When shaken with concentrated sulphuric acid, the resulting mixture becomes brown, heat also being given off; on the addition of water it becomes colourless, and an oil rises to the surface which on cooling becomes quite thick. The thick oily product, which is, probably, the polymerised hydrocarbon, is nearly insoluble in alcohol.

Fuming nitric acid acts violently on this hydrocarbon and dissolves it. On the addition of water a yellow oil separates, becoming quite thick on cooling.

Dibromide of Isopropylbutenylbenzene, $C_{13}H_{18}Br_2$.—This is prepared in the same manner as the dibromide of isopropylallylbenzene. It melts at 77°. On analysis it gave the following numbers:—

·2426 of substance gave
·4122 of CO_2, and
·1194 of H_2O.

	Theory for $C_{13}H_{18}Br_2$.	Experiment.
Carbon	46·70	46·33
Hydrogen	5·38	5·46

This substance is very soluble in benzol, ether, and petroleum spirit. It also dissolves freely in boiling alcohol, and is deposited from it on cooling in transparent plates. Heated with an alcoholic solution of potassium hydrate it decomposes, yielding potassium bromide and a brominated oil.

Allylbenzene.

This hydrocarbon has an odour similar to cinnamene. It boils at 174—175°, and has a sp. gr. at 15° of ·9180.* When heated between 160° and 200° for sixty hours it did not undergo any visible change. It does not freeze at − 15°. On analysis it gave the following numbers:—

·1928 of substance gave
·6451 of CO_2, and
·1464 of H_2O.

	Theory for C_9H_{10}.	Experiment.
Carbon	91·52	91·25
Hydrogen	8·47	8·43

---

* Freshly prepared cinnamene has a density of ·912 at 15°.

The constitution of this hydrocarbon may be represented thus:—

$$C_9H_{10} = C_6H_5.CH{=}CH.CH_3.$$

This hydrocarbon, when treated with concentrated sulphuric acid, produces a yellow coloration in the acid, but does not dissolve to any appreciable extent; it becomes changed, however, and on the dilution of the acid rises to the surface as an oily layer, which becomes thick on cooling. Boiled with dilute nitric acid it becomes yellow, and heavier than water, red fumes being given off.

Dibromide of Allylbenzene, $C_9H_{10}Br_2$.—Allylbenzene, when treated with bromine water in excess, produces a heavy oil. This, after washing with a little alkali, does not solidify easily; it is therefore best to cool it in a freezing mixture, which quickly causes it to become a crystalline mass; this does not become fluid again on acquiring the ordinary atmospheric temperature. It is purified by pressure between calico and crystallisation from alcohol. On analysis it gave the following numbers:—

·2590 of substance gave
·3679 of CO_2 and
·0880 of H_2O.

	Theory for $C_9H_{10}Br_2$.	Experiment.
Carbon	38·84	38·72
Hydrogen	3·59	3·77

This substance is easily soluble in hot alcohol, and crystallises from it on cooling in needles. It melts at 67°. When treated with hot alcoholic potassium hydrate, it yields potassium bromide and a brominated oil.

Butenylbenzene.

This substance is a colourless oil boiling at 186—187° C. Its odour is somewhat similar to cinnamene. Its analysis gave the following numbers:—

·2153 of substance gave
·7171 of CO_2 and
·1750 of H_2O.

	Theory for $C_{10}H_{12}$.	Experiment.
Carbon	90·9	90·83
Hydrogen	9·1	9·02

The constitution of this substance may be represented thus:—

$$C_{10}H_{12} = C_6H_5.CH{=}CH.CH_2.CH_3.$$

Dibromide of Butenylbenzene, $C_{10}H_{12}Br_2$.—Butenylbenzene, when treated with bromine water, behaves just in the same manner as allylbenzene. The crude oily dibromide solidifies when cooled, and is then purified by pressure and crystallisation from alcohol. It crystallises in needles, melting at 67°. With alcoholic potash, it decomposes with formation of potassium bromide and a brominated oil.

Allyl- and butenylbenzenes have already been obtained. The first was produced in small quantities in the preparation of phenylpropylalcohol by the action of nascent hydrogen on cinnamic alcohol by L. Rügheimer (*Journ. Chem. Soc.*, 1874, p. 894). This product is without doubt, identical with that described above, although the boiling point given is low, but the fusing point of the dibromide only differs by half a degree.

Fittig has shown that this product should have the same constitution as that I have given to my product, which is seen from its method of production—

$$\underset{\text{Cinnamic alcohol.}}{C_6H_5.CH{=}CH.CH_2OH} + H_2 = \underset{\text{Allyl benzene.}}{C_6H_5.CH{=}CH.CH_3} + OH_2.$$

The butenylbenzene, however, which was produced by the action of sodium on a mixture of benzylchloride and allyl iodide by B. Aronheim (*Deut. Chem. Ges. Ber.*, v, 1068), is evidently isomeric with the one I have prepared, its constitution being expressed thus :—

$$C_6H_5.CH_2.CH_2.CH{=}CH_2.$$

In a previous paper, I mentioned that the acids I had obtained from anisic aldehyde, if strongly heated, decompose, with formation of carbonic anhydride and oily products, one of which was supposed to be anethol, and the others homologues of that substance. (*Journ. Chem. Soc.*, 1877, pp. 409, 412, 413). I now give the results obtained by a further investigation of the subject.

Paravinylanisoïl.

On gently boiling methylparoxyphenylacrylic acid in a large bulb-tube having a side-delivery tube, an oil gradually distils over, having an odour similar to that of fennel. The crude product obtained in this way was purified first by washing with dilute potassium hydrate and then by distillation with water. It was finally dried over anhydrous sodium carbonate, and on analysis gave the following numbers :—

I. ·209 of substance gave
·6325 of CO_2 and
·141 of H_2O.
II. ·193 of substance gave
·57075 of CO_2 and
·131 of H_2O.

	Theory for $C_9H_{10}O$.	Experiment. I.	Experiment. II.
Carbon	80·59	80·38	80·64
Hydrogen........	7·40	7·49	6·51

The formation of this body, which I propose to call *paravinylanisoïl*,* may be expressed thus :—

$$C_6H_4(OCH_3).CH{=}CH.COOH = C_6H_4(OCH_3).CH{=}CH_2 + CO_2.$$

Methylparoxyphenylacrylic acid. Paravinylanisoïl.

This substance boils at about 201—202°, but during its distillation a large quantity changes and becomes viscid, and on cooling solidifies to a transparent mass. Heated to 150° for a few hours, it also changes into this substance. This compound, which is undoubtedly polymerised paravinylanisoïl, volatilises when strongly heated, an oil, apparently paravinylanisoïl, distilling over.

When cooled in a freezing mixture, paravinylanisoïl solidifies to a perfectly hard crystalline mass, melting at about — 1—2°.

Paravinylanisoïl when agitated with bromine-water, produces a white fusible derivative. With concentrated sulphuric acid, it becomes dark red and nearly solid, heat being given off. On adding water, the colour first changes to purple; but on the application of heat this disappears, white flakes being left, apparently consisting of a polymerised product.

An endeavour was made to produce this anethol by Binder's reaction; but on treating methylparoxyphenylacrylic acid with fuming hydrobromic acid, it at first became a soft resinous mass, and on opening the tube in which the mixture had been kept, a small quantity of gas escaped, and the solution effervesced, apparently owing to the volatilisation of bromide of methyl. The solid product when treated with sodium carbonate, did not yield any volatile product.

Anethol or Parallylanisoïl.

On heating methylparoxyphenylcrotonic acid in a long-necked bulb-retort, an oil gradually distils over, carbonic anhydride being also given off. This oil was washed with caustic alkali to remove any unchanged acid which had distilled over with it, and then distilled with water. After being dried with anhydrous sodium carbonate, it was fractionally distilled; ebullition commenced at about 220°, the principal quantity, however, coming over between 230—240°, and leaving a small residue of high boiling point. Both of these fractions solidified when cooled in a freezing mixture, but the higher one froze more readily and became the harder of the two. On pressing these products between bibulous paper in a press cooled with ice, a white crystalline mass was obtained, and was further purified by crystallisation from alcohol. This substance proved to be perfectly pure anethol. The oily impurity with which it is associated in the crude product of the distillation of methylparoxyphenylcrotonic acid, has not been examined, as it seems impossible to free it from anethol, which is excessively soluble in it. I am, therefore, unable to judge whether it is a liquid modification of that substance, or simply anethol kept in solution by a small amount of some other substance.

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* Anethol and its homologues are para-derivatives of anisol. Anisol being an ether, the termination *ol* is undesirable, being now used for phenols. It is therefore proposed to replace it by oïl,—thus, anisoïl instead of anisol.

On treating methylparoxyphenylcrotonic acid with fuming hydrobromic acid, sp. gr. 1·76, for several days, it was found to combine; the resulting additive product is, however, very unstable, decomposing even when washed with water, and becoming a viscid mass. I was not able to get it in a fit state for analysis.

The crude acid simply drained from the hydrobromic acid was treated with sodium carbonate and well-stirred: decomposition then took place, and the smell of anethol became evident. The mixture was warmed, when an oily layer formed on its surface; this was collected and distilled with water. The oily product was found to be perfectly pure anethol, solidifying to a crystalline mass on cooling.

The following numbers were obtained on the analysis of this substance obtained by the above processes, No. I being that of a specimen prepared by heating methylparoxylphenylcrotonic acid; II, that of a specimen made from the additive product:—

I. ·2408 of substance gave
·7143 of CO_2 and
·1730 of H_2O.
II. ·1864 of substance gave
·5542 of CO_2 and
·1376 of H_2O.

	Theory for $C_{10}H_{12}O$.	Experiment. I.	Experiment. II.
Carbon	81·08	80·94	81·06
Hydrogen	8·10	7·98	8·20

The identity of this body with anethol obtained from oil of anise was established by a comparison of the boiling and fusing points of the two products, which were found to be identical, as also by their specific gravities, which were as follows:—

Artificial anethol, at 30°	·9852
Natural „ „	·9858

The odour, taste, and appearance of the two substances were also the same.

The formation of this substance may be expressed thus :—

I. $C_6H_4(OC\overset{p}{H}_3).CH{=}CH.CH_2.COOH = C_6H_4(OC\overset{p}{H}_3).CH{=}CH.CH_3$
Methylparoxyphenylcrotonic acid. Anethol.
$+ CO_2$.

II. $C_6H_4(OC\overset{p}{H}_3).CH_2.CHBr.COOH + C_6H_4(OC\overset{p}{H}_3).CH{=}CH.CH_3$
Hydrobromomethylparoxyphenylcrotonic acid. Anethol.
$+ HBr + CO_2$.

Parabutenylanisoïl.

This substance may be obtained in an impure state by distilling methyl-paroxyphenyl-angelic acid; but by employing the hydrobromo-derivative of that acid, and treating it with sodium carbonate, &c., as in the preparation of anethol, it is obtained perfectly pure. The preparation of hydrobromomethylparoxyphenylcrotonic acid is effected in the usual way. It has not been analysed.

Parabutenylanisoïl is a beautifully crystalline substance melting at 17° C. In odour and taste it is similar to ordinary anethol. It boils at 242—245°. Its sp. gr. at 30° is ·9733. On analysis it gave the following numbers :—

I. ·2358 of substance gave
·7017 of CO_2 and
·1812 of H_2O.
II. ·2227 of substance gave
·6651 of CO_2 and
·1734 of H_2O.

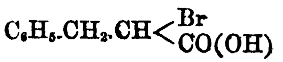
	Theory for $C_{11}H_{14}O$.	Experiment. I.	II.
Carbon	81·48	81·15	81·45
Hydrogen	8·64	8·53	8·64

The formation of this substance may be expressed thus:

$$C_6H_4(OCH_3)CH_2.CHBr.CH_2.CH_2COOH =$$
Hydrobromomethylparoxyphenylcrotonic acid.

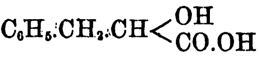
$$C_6H_4(OCH_3).CH{=}CH.CH_2CH_3 + HBr + CO_2.$$
Parabutenylanisoïl.

The constitution of hydrobromo cinnamic acid is represented thus—



$$C_6H_5.CH_2.CH{<}\begin{matrix}Br\\CO(OH)\end{matrix}$$

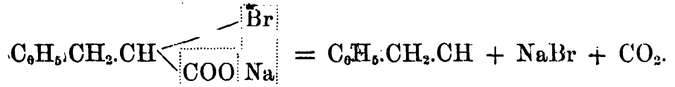
because it is identical with the acid which Glaser obtained by treating phenyllactic acid with hydrobromic acid, the constitution of phenyllactic acid being represented as—



$$C_6H_5.CH_2.CH{<}\begin{matrix}OH\\CO.OH\end{matrix}$$

I have therefore assigned to the analogous acids described in this paper a similar structure.

The explanation given of the formation of cinnamene from hydrobromocinnamic acid by the action of sodium carbonate is that a sodium salt is first produced; and that this salt suffers an intra-molecular change in consequence of the affinity of the bromine for the sodium, sodium bromide being formed, and the combining unit of the one oxygen-atom which is set free loosening the carbon-atom of the carboxyl group from the chain, thus:—



$$C_6H_5.CH_2.CH{<}\begin{matrix}Br\\COO\ Na\end{matrix} = C_6H_5.CH_2.CH + NaBr + CO_2.$$

This, however, represents cinnamene as having a constitution at variance with that generally accepted, viz., $C_6H_5.CH.CH_2$, which is so clearly indicated by the decomposition of cinnamic acid by heat.

But in order to obtain hydrocarbons from the hydrobromo-acids, I have found that it is not necessary to treat them with sodium carbonate or other alkaline products, which would convert them into salts. A dilute aqueous solution of silver nitrate will answer the purpose, silver bromide, carbonic anhydride, and the hydrocarbon being produced. Sodium acetate also, in presence of a large excess of acetic acid may also be used, the mixture when warmed, yielding abundance of carbonic anhydride, and the hydrocarbon soon collecting and forming an oily layer on the surface of the liquid. This process appears to give quite as large a yield of product as when sodium carbonate is employed. Other salts may also be used, in fact, nearly any compound which has an affinity for hydrobromic acid appears to answer. In some cases, as that of hydrobromocumenyl-crotonic acid, a certain amount of hydrocarbon is obtained on simply boiling the acid with water.

The tendency of these additive acids is to give up hydrobromic acid, and usually, instead of regenerating the acid they were prepared from, they yield hydrocarbons and carbonic anhydride. If a sodium salt be formed when these acids are treated with sodium carbonate, on the separation of hydrobromic acid from the compound, we should get bromide of sodium and cinnamic acid, or its products of decomposition, together with carbonic anhydride and cinnamene, which according to this would have the constitution usually assigned to it.

It is mainly from these considerations that I have expressed the formation of the hydrocarbons and derivatives of anisoïl as resulting simply from the separation of hydrobromic acid and carbonic anhydride from the hydrobromo-acids. This view is also consistent with that of their formation from the non-hydrobrominated acids by the action of heat.

It is remarkable that the hydrocarbons and paravinylanisoïl, compounds which contain vinyl, C_2H_3, are the only ones which polymerise when heated, and form products corresponding to metacinnamene. They are also remarkable on account of their boiling points, the difference between them and the compounds containing allyl being so much greater than between the allyl and butenyl compounds. This will be seen from the following table, using the highest numbers:—

		B. p.	Difference.
I.	Cinnamene, or Vinyl-benzene......	144·5°	= 26·5°
	Allyl-benzene....................	170—171°	
	Butenyl-benzene	186—187°	= 16·0°
II.	Isopropylvinyl benzene	203—204°	= 26·0°
	Isopropylallyl benzene............	229—230°	
	Isopropylbutenyl benzene	242—243°	= 13·0°
III.	Paravinylanisoïl	204—205°	= 27·0°
	Paraallylanisoïl (anethol)	232°	
	Parabutenylanisoïl	242—245°	= 13·0°

The boiling points of these substances were taken with small quantities of material, otherwise still more concordant results would probably have been obtained.

I hope shortly to give an account of some isomeric derivatives of anisoïl in which the replacement is in the ortho position.

The following is a list of substances which have been analysed, and are described in this paper:—

Hydrobromocumenyl-acrylic acid—

$C_{12}H_{15}BrO_2 = C_6H_4(C_3H_7).CH_2.CHBr.CO(OH).$

Hydrobromocumenyl-crotonic acid—

$C_{13}H_{17}BrO_2 = C_6H_4(C_3H_7).CH_2.CHBr.CH_2.CO(OH).$

Hydrobromocumenyl-angelic acid—

$C_{14}H_{19}BrO_2 = C_6H_4(C_3H_7).CH_2.CHBr.CH_2.CH_2.CO(OH).$

Allylbenzene—

$C_9H_{10} = C_6H_5.CH.CH.CH_3.$

Allylbenzene dibromide—

$C_9H_{10}Br_2 = C_6H_5.CHBr.CHBr.CH_3.$

Butenylbenzene—

$C_{10}H_{12} = C_6H_5.CH.CH.CH_2.CH_3.$

Isopropylvinyl-benzene—

$$C_{11}H_{14} = C_6H_5\left\{\begin{array}{l}CH.CH_2\\ CH.(CH_3)_2.\end{array}\right.$$

Isopropylvinyl-benzene dibromide—

$$C_{11}H_{14}Br_2 = C_6H_5\left\{\begin{array}{l}CHBr.CH_2Br\\ CH(CH_3)_2\end{array}\right. .$$

Isopropylallyl-benzene—

$$C_{12}H_{16} = C_6H_5\left\{\begin{array}{l}CH.CH.CH_3\\ CH.(CH_3)_2\end{array}\right. .$$

Isopropylallyl-benzene dibromide—

$$C_{12}H_{16}Br_2 = C_6H_5\left\{\begin{array}{l}CHBr.CHBr.CH_3.\\ CH.(CH_3)_2\end{array}\right.$$

Isopropylbutenyl-benzene—

$$C_{13}H_{18} = C_6H_9\left\{\begin{array}{l}CH.CH.CH_2CH_3\\ CH.(CH_3)_2\end{array}\right. .$$

Isopropylbutenyl-benzene dibromide—

$$C_{13}H_{18}Br_2 = C_6H_5\left\{\begin{array}{l}CHBr.CHBr.CH_2.CH_3\\ CH.(CH_3)_2\end{array}\right. .$$

Paravinylanisoïl—

$$C_6H_4(OC\overset{p}{H}_3).CH=CH_2.$$

Parallylanisoïl—

$$C_6H_4(OC\overset{p}{H}_3).CH=CH.CH_3.$$

Parabutenylanisoïl—

$$C_6H_4(OC\overset{p}{H}_3).CH=CH.CH_2.CH_3.$$

XXIX.—*On two New Methods for Estimating Bismuth Volumetrically.*

By M. M. PATTISON MUIR, F.R.S.E.

1. IN the *Journal* of the Society (vol. i, 1876, p. 483) will be found a paper in which I describe a process for the volumetric determination of bismuth. This process is based upon the insolubility of bismuthyl dichromate in neutral or nearly neutral liquids, and upon the ease with which the smallest quantity of a soluble chromate may be detected, by taking advantage of the production of red chromate of silver. An additional note modifying and, I think, improving, this process, appeared in vol. i, 1877, p. 658.

Although the dichromate process gave very good results, yet it was rather uncertain in its action. I have made very many attempts to devise a process for the volumetric estimation of bismuth, which should be rapid in execution, and definite and trustworthy in results. I think that I have at last succeeded.

2. Chancel (*Jahresbericht*, 1860, p. 612) has shown that bismuth is completely precipitated from solutions containing nitric acid, but free from hydrochloric and sulphuric acids, by addition of sodium phosphate. The precipitate has the composition $BiPO_4$: it is not decomposed by boiling with very dilute nitric acid.

As small quantities of a soluble phosphate may be detected in solutions containing nitric acid by means of the ammonium molybdate test, the reaction observed by Chancel appeared to be one upon which a good method for determining bismuth volumetrically might be based.

3. A liquid containing a known quantity of bismuthous oxide, dissolved in nitric acid, was prepared; a dilute solution of pure sodium phosphate was also prepared. A measured quantity of the bismuth solution was mixed with ammonia until a slight precipitate appeared, the liquid was heated to boiling, dilute nitric acid was added until the precipitate had completely dissolved, and the sodium phosphate solution was run in from a burette. After each addition of a few drops of the phosphate solution, the contents of the beaker were boiled for a moment, the precipitate was allowed to settle, and a drop of the supernatant liquid was spotted on a white slab, where it was brought into contact with a drop of a warm solution of ammonium molybdate in nitric acid. So soon as a faint yellow turbidity was produced on the slab, the precipitation of bismuth phosphate was regarded as complete. The following numbers were obtained:—

10 cb.c. bismuth solution = 0·0654 gram Bi required 7·5 cb.c. sodium phosphate solution.

10 cb.c. bismuth solution = 0·0654 gram Bi required 7·7 cb.c. sodium phosphate solution.

20 cb.c. bismuth solution = 0·1308 gram Bi required 15·5 cb.c. sodium phosphate solution.

25 cb.c. bismuth solution = 0·1635 gram Bi required 18·3 cb.c. sodium phosphate solution.

25 cb.c. bismuth solution = 0·1635 gram Bi required 18·5 cb.c. sodium phosphate solution.

10 cb.c. bismuth solution = 0·0654 gram Bi required 7·7 cb.c. sodium phosphate solution.

10 cb.c. bismuth solution = 0·0654 gram Bi required 7·8 cb.c. sodium phosphate solution.

10 cb.c. bismuth solution, mixed with a fresh quantity of nitric acid, then treated as before, required 7·7 cb.c. sodium phosphate solution.

Taking the average of these results, we have 7·6 cb.c. phosphate solution = 0·0654 gram Bi, or 1 cb.c. phosphate = 8·605 milligm. bismuth.

If the amounts of bismuth found be calculated on this basis, the following results are obtained:—

	Bismuth taken. Milligrams.	Bismuth found. Milligrams.	Difference. Milligrams.
(1)	65·4	64·53	−0·87
(2)	65·4	66·25	+0·85
(3)	130·8	133·37	+2·57
(4)	163·5	157·5	−6·00
(5)	163·5	159·2	−4·3
(6)	65·4	66·25	+0·85
(7)	65·4	67·12	+1·72
(8)	65·4	66·25	+0·85

4. These results show that this process is only approximately accurate. By making the phosphate solution considerably more dilute, much better results might doubtless have been obtained. The final reaction is scarcely so decisive as might be desired. But the main reason why the process was not so successful as might have been anticipated is, in my opinion, the fact that an excess of sodium phosphate above the theoretical quantity required for completing the reaction, is really needed in order to precipitate the whole of the bismuth, and that this excess appears to increase slightly, the greater the amount of bismuth to be thrown down.

The amount of phosphoric acid in the sodium phosphate employed was determined by titration with standard uranium acetate solution: 1 cb.c. phosphate was found to be equal to 3·7 mgm. P_2O_5. Now 65·4 mgm. of bismuth should require 22·1 mgm. P_2O_5 for complete precipitation (P_2O_5 = 2Bi): they actually required 28·12 mgm., or an excess of 6·02 mgm. 130·8 mgm. bismuth should require 44·2 mgm. P_2O_5; the actual amount of P_2O_5 added was 57·35 mgm., or an excess of 13·15 mgm. P_2O_5. On the supposition that doubling the amount of bismuth to be precipitated would necessitate twice as large an excess of phosphate, 130·8 mgm. of bismuth would have required an excess of P_2O_5 amounting to 12·04 mgm., but the excess actually needed amounted to 13·15 mgm. Of course these figures are based on the assumptions that the smallest excess of phosphoric acid was detected by the molybdate reaction, and that the different determinations were carried out under exactly similar conditions. Looking at these experiments as a whole, I am inclined to believe that the process sketched above might be made to yield very fairly accurate results; but, as the method to be described in the sequel is so very accurate, and at the same time so easily carried out, I have not cared to spare the time which would be necessary for perfecting the precipitation method.

5. The uranium process for determining phosphoric acid is well

known, and is thoroughly trustworthy. If bismuth is completely precipitated by addition of an excess of sodium phosphate, and if the precipitate is of constant composition, it will be easy to determine this metal volumetrically by employing a measured volume—excess—of standard sodium phosphate solution, and determining the amount of phosphoric acid remaining in solution when the action is complete. This is the principle upon which my second method is based.

It was only necessary for me to convince myself by experimental proof that the *whole* of the bismuth is precipitated from a solution of that metal in nitric acid, when the solution is treated with an excess of sodium phosphate: that the precipitate formed is of definite composition, and is not altered in composition by any of the conditions under which it may be brought during the carrying out of the process, and what the composition of the precipitate is, or at any rate what is the proportion between bismuth and phosphoric acid in the precipitate. If these points were satisfactorily settled, the process would of necessity be successful.

I have convinced myself that, from a solution of bismuth in nitric acid made nearly neutral with ammonia, *or mixed with an excess of sodium acetate*, the *whole* of the bismuth is thrown down on boiling for a few, minutes with an excess of sodium phosphate; that the relation between bismuth and phosphoric acid in the precipitate remains perfectly constant during ebullition, independently of the amount of nitric acid originally present, provided that amount be sufficient to maintain the whole of the bismuth in solution, and provided that an excess of sodium acetate be added before the addition of sodium phosphate; and lastly, that the relation between bismuth and phosphoric acid in the precipitate is as Bi : PO_4, or that P_2O_5 precipitates 2Bi.

6. The following numbers show that the process really succeeds—

0·1545 gram bismuth dissolved in nitric acid was mixed with a considerable excess of sodium acetate solution; the liquid was heated to boiling; 10 cb.c. of a sodium phosphate solution, each cb.c. of which was equal to 22·6035 mgm. P_2O_5, were run in; the liquid was boiled for a few minutes, and then filtered; the precipitate was washed several times with hot water; and phosphoric acid was determined in the filtrate by means of standardised uranium solution. This experiment was repeated three times.

The number of cb.c. of uranium solution used was: No. 1, 49·0; No. 2, 49·0; No. 3, 49·1. 6·37 cb.c. of uranium solution were equal to 1 cb.c. of the phosphate solution; the amount of phosphate solution required to precipitate the whole of the bismuth was therefore 2·31 cb.c.: this is equal to 0·1555 gram Bi.

Taken.	Found.	Difference.
0·1545 gram	0·1555 gram	+0·001 gram

Many other experiments were performed in order to arrive at a knowledge of the conditions most favourable for carrying out the process.

I do not propose to detail these experiments, but rather to state their general results in the form of directions for carrying out the volumetric estimation of bismuth by the phosphate method.

7. The standard liquids required are—

(1.) *A solution of pure sodium phosphate*, preferably $\frac{1}{20}$ normal* (1 cb.c. = 7·1 mgm. P_2O_5) prepared by dissolving 35·8 grams of the recrystallised salt in 1000 cb.c. of water.

(2.) *A solution of uranium acetate* of a strength such that 1 cb.c. is equal to 1 cb.c. of the phosphate solution: prepared by dissolving about 16 to 18 grams of yellow uranium oxide in 1000 cb.c. of dilute acetic acid, titrating against the standard phosphate by the ordinary method, and diluting until of the proper strength.

The bismuth to be estimated must be dissolved in nitric acid: bases other than the alkalis and alkaline earths must be absent. The absence of those acids which interfere with the determination of phosphoric acid by the uranium process (non-volatile, and reducing organic acids, sulphuretted hydrogen, hydriodic acid, &c.) must be assured. As bismuth is readily separated from other metals, with the exception of antimony and tin, by addition of much warm water and a little ammonium chloride to feebly acid solutions, a separation of the bismuth from those other metals which are present should precede the process of estimation. If alkalis or alkaline earths be alone present, the separation may be dispensed with. The precipitated bismuth salt is to be washed, dissolved in a little strong nitric acid, and the solution boiled down twice with addition of a little more nitric acid, in order to remove the whole of the hydrochloric acid present.

Such a quantity of a tolerably concentrated solution of sodium acetate is added as shall insure the neutralisation of the nitric acid, and therefore the presence in the liquid of free acetic acid. If a precipitate form, a further addition of sodium acetate must be made. The liquid is heated to boiling; a measured volume of the sodium phosphate solution is run in; the boiling is continued for a few minutes; the liquid is passed through a ribbed filter, the precipitate being washed repeatedly with hot water; and excess of phosphoric acid is determined in the filtrate by titration with uranium. If the filtered liquid be received in a measuring flask, which is subsequently filled to the mark with water, and if the inverted uranium method of Fresenius be then employed, the results are exceedingly accurate; this method is especially to be recommended in the estimation of somewhat large quantities of bismuth, inasmuch as it is possible that much sodium acetate will in such cases have been used, and it is well known that the presence of a large excess of alkaline acetates interferes with the accuracy of the uranium method as generally carried out, but is without influence if the inverted method be adopted.

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* I have regarded a solution containing P_2O_5 in grams per litre as normal.

If the bismuth solution contains a large excess of nitric acid, it is better to add sodium carbonate until a slight precipitate forms, to dissolve this by addition of a very little nitric acid, and to proceed in the manner described.

XXX.—*On the Volumetric Estimation of Mercury.*

By RICHARD V. TUSON, Professor of Chemistry and Toxicology in the Royal Veterinary College, and EDMUND NEISON.

IN the *Journal of the Chemical Society* for June, 1873 (vol. xxvi, p. 565), Hannay described a method of estimating mercury volumetrically by means of ammonium hydrate and potassium cyanide; but as employed by him the process was restricted to the determination of the amount of metal in pure aqueous solutions of mercuric chloride. During the progress of an investigation instituted by the former of us, on the digestion (solubility) of calomel by pepsin and dilute hydrochloric acid (*The Lancet*, August 13th, 1870), it became necessary to make a considerable number of determinations of mercury in various mercuric and mercurous compounds, and we were consequently led to examine the different methods devised for this purpose. The process which seemed to offer the greatest facilities for rapid and yet accurate work, especially when the amount of mercury was small, was that invented by Hannay. Before, however, it could be considered capable of general application, it was found essential to subject the method to careful investigation. This task we have at all events partially accomplished, and we now beg to lay before the Society the results of our inquiry.

The method of estimating mercury by Hannay's process is very simple. A known volume of the mercury solution under examination is taken; a few drops of dilute ammonium hydrate are added; and the white precipitate which forms is dissolved by running in a standard solution of potassium cyanide until the last trace of opalescence disappears. Towards the end of the operation the solution is carefully stirred for about half a minute after each addition of potassium cyanide. For the purpose of exactly ascertaining the vanishing point of the opalescence, the experiment should be performed in a beaker standing on some dull black material, such as a piece of black velvet. If the operation be properly conducted, and the potassium cyanide pure, the disappearance of the last trace of opalescence is easily observed, and the end of the process thereby sharply marked. The peculiar blue opalescence presented by the liquid when nearly the exact amount of potassium cyanide has been added, is so characteristic, that its disappearance can be readily seen, even in the presence of traces of the grey precipitate arising from impurities in the cyanide, with which the solution is sometimes contaminated.

The following are the standard solutions employed:—

Standard Solution of Mercuric Chloride.—13·55 grams of pure mercuric chloride are dissolved in 1 litre of water. 1 c.c. of this solution contains 0·01 gram of mercury.

Standard Solution of Potassium Cyanide.—17 grams of pure crystallised potassium cyanide are dissolved in 1 litre of water, and the solution thus produced is titrated with 10 c.c. of the standard solution of mercuric chloride. If x be the volume of cyanide requisite to remove the last trace of opalescence, then $10 - x$ c.c. of water must be added to every x c.c. of the remainder of potassium cyanide solution to standardise it.

When of proper strength, 1 c.c. is equal to 1 c.c. of the standard solution of mercuric chloride.

In addition to the foregoing, it is useful to have a solution of 1 part of strong ammonia in 10 parts of water, a solution of 5·36 grams of ammonium chloride in 1 litre of water, and a solution of 69 grams of potassium carbonate in 1 litre of water.

When the amount of mercury to be estimated is small, or great accuracy is required, a weaker solution of potassium cyanide than the one above referred to should be employed. It may be formed by diluting from 50 to 100 c.c. of the standard to 1 litre. The potassium cyanide solutions keep fairly well for several months, and when they have lost strength, fresh solutions can be easily prepared, or the old ones may be readily re-standardised.

The following experiments illustrate the process, and indicate the delicacy and accuracy of the results obtainable by it:—

α. 50 c.c. of a solution of mercuric chloride containing 0·1933 gram of the salt were taken, and the mercury estimated.

Potassium cyanide solution used, 14·25 c.c. = 0·19305 gram of $HgCl_2$.

β. Another 50 c.c. of the same solution of mercuric chloride were divided into five quantities of 10 c.c., and the mercury estimated in each.

Potassium cyanide solution (*decinormal*) used, 28·65 c.c., 28·5 c.c., 28·52 c.c., 28·48 c.c., and 28·58 c.c.; total 142·73 c.c. = 0·19334 gram of $HgCl_2$.

γ. 50 c.c. of a solution of mercuric chloride containing 0·02134 gram of the salt were taken, and the mercury estimated.

Potassium cyanide solution (*decinormal*) used, 15·78 c.c. = 0·02138 gram of $HgCl_2$.

δ. Another 50 c.c. of the same solution of mercuric chloride as the last were divided into five quantities of 10 c.c., and the mercury estimated in each.

Potassium cyanide solution (decinormal, diluted with its own volume of water) used, 6·35 c.c., 6·25 c.c., 6·29 c.c., 6·38 c.c., and 6·33 c.c.; total 31·6 = 0·021385 gram of $HgCl_2$.

ε. 50 c.c. of a solution of mercuric chloride, containing 0·00271 gram of the salt were taken, and the mercury estimated.

Potassium cyanide solution (centinormal) used, 19·8 c.c. = 0·002683 gram of $HgCl_2$.

ζ. Another 50 c.c. of the same solution of mercuric chloride as the last were divided into five quantities of 10 c.c., and the mercury estimated in each.

Potassium cyanide solution (centinormal) used, 3·7 c.c., 3·95 c.c., 4·4 c.c., 3·7 c.c., and 4·2 c.c.; total 19·95 c.c. = 0·002703 gram of $HgCl_2$.

It will now be seen that extremely small quantities of mercury may be accurately estimated by Hannay's method; in fact, a fraction of a milligram of this metal may be determined to within 2 or 3 per cent. of the actual amount present in a solution of pure mercuric chloride by a single experiment.

It, however, appeared to us probable that the presence of considerable quantities of ammonium salts would materially interfere with the applications of the process, and experiment at once proved such to be the case.

Influence of Ammonium Chloride.—In presence of large quantities of ammonium chloride, it was found that ammonium hydrate gave no precipitate with small quantities of mercuric chloride; and even with smaller amounts of ammonium chloride the precipitate that formed presented anomalies which rendered the process unreliable. Numerous experiments were made to determine what quantity of ammonium salt might be present without exerting a prejudicial effect. It was then found that any amount of ammonium chloride under 15 times the weight of mercury-compound present appeared to exert but little influence, but that a quantity of ammonium chloride exceeding 25 times that of the mercury salt materially interfered with the process.

Influence of Ammonium Nitrate.—Large quantities of this salt were found to exert an influence similar to that produced by the chloride, *i.e.*, they prevented the formation of a mercury precipitate with ammonium hydrate. Repeated experiment showed that a quantity of ammonium nitrate equal to 25 times the weight of mercury salt entirely prevented the formation of any precipitate by ammonium hydrate, and that the quantity of ammonium salt necessary for this purpose was approximatively inversely as the concentration of the solution of the mercury salt. The amount of ammonium nitrate present should not exceed ten times the weight of the mercury salt; with smaller quantities of nitrate but little influence seemed to be exercised.

Influence of Ammonium Sulphate.—A long series of experiments was tried with this salt, and results were obtained which were very similar to those yielded with the chloride and nitrate. When the weight of ammonium sulphate was 25 times that of the mercury salt, no precipitate formed on the addition of ammonium hydrate. So long as the amount of ammonium sulphate did not exceed ten times that of the mercury salt, the accuracy of the method was not interfered with.

The explanation of the fact that a quantity of an ammonium salt equal to ten times the weight of mercury-compound may be present without affecting the process, whilst double this quantity of ammonium salt precludes its adoption, apparently exists in the circumstance that ammonium salts act entirely by preventing the formation of the precipitate by ammonium hydrate. For after this precipitate is formed, much larger quantities of ammonium salts than those above named are required to dissolve it, except after an inconvenient length of time.

Influence of Potassium and Sodium Salts.—The results obtained with ammonium salts were important, for we proposed to neutralise acid solutions containing mercury with ammonium hydrate as a preliminary to the application of Hannay's process.

It soon became evident, however, that unless the amount of mercury was known to be large, or the acidity of the solution very slight, this mode of neutralisation could not be adopted. Moreover, in separating certain other metals which might co-exist with the mercury, it would be necessary to introduce ammoniacal salts, and a prejudicial amount of them would be formed, in most cases where highly acid solutions had to be neutralised by ammonium hydrate.

It is likewise worthy of note that evaporation cannot be resorted to as a means of expelling any excess of acid that may exist in mercurial solutions, on account of the substantial loss of mercury to which it gives rise.

We next endeavoured to ascertain whether or not the sulphates, nitrates, chlorides, or acetates of potassium or sodium would interfere with [illegible] precipitation of mercury by ammonia, when it was found that a quantity of either of these salts amounting to one thousand times the weight of the mercury salt was without influence on the process. It was, however noticed, that both potassium and sodium hydrate appear to impart a persistency to the precipitate, and to render the last traces of it difficultly soluble in potassium cyanide.

Potassium carbonate and sodium carbonate were without action. Accordingly an acid solution of mercury may be readily brought into a fit condition for the application of Hannay's process by neutralising it with potassium or sodium carbonate. If large quantities of ammonium salts be present, they can be easily removed by adding potassium hydrate, and gently boiling, until ammonia is no longer evolved. No loss of mercury occurs in this operation.

The general method employed by us for determining the amount of metal in any soluble salt of mercury was to add a small quantity of solution of ammonium chloride and then potassium carbonate, until an opalescent precipitate made its appearance. Standard solution of potassium cyanide was then run in, with constant stirring, until the precipitate dissolved, and the solution became perfectly clear. Compounds of mercury insoluble in water were dissolved in nitric, hydrochloric, or sulphuric acid, a small quantity of ammonium chloride solution added, and then solution of potassium carbonate, until the characteristic white opalescent precipitate formed. Mercury compounds insoluble in the above-named acids were dissolved in nitro-hydrochloric acid, and treated with ammonium chloride, &c., as before. The following analyses were performed in this manner:—

Mercuric Nitrate.—A solution of mercuric nitrate in nitric acid, and containing 1·62 gram of the salt per litre, was taken, and the following analyses conducted:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric nitrate.		
		Found.		Used.
		Gram.		Gram.
5 c.c.	4·995 c.c.	0·008092	0·016289	0·0162
5 „	5·070 „	0·008197		
25 „	25·030 „	0·040549	0·081130	0·0810
25 „	25·050 „	0·040581		

Mercuric Sulphate.—A solution containing 1·48 gram of this salt per litre (in dilute sulphuric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric sulphate.		
		Found.		Used.
		Gram.		Gram.
10 c.c.	9·96 c.c.	0·014741	0·044414	0·0444
10 „	10·03 „	0·014844		
10 „	10·02 „	0·014829		
50 „	49·96 „	0·073940	0·222134	0·222
50 „	50·08 „	0·074120		
50 „	50·05 „	0·074074		

Mercuric Acetate.—A solution containing 3·18 grams of this salt per litre (in acetic acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric acetate.		
		Found.		Used.
		Gram.		Gram.
25 c.c.	25·25 c.c.	0·080295	0·160378	0·159
25 „	25·18 „	0·080083		

Mercuric Oxalate.—A solution containing 5·71 grams of this salt per litre (in hydrochloric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	cyanide used.	Mercuric oxalate.		
		Found.		Used.
		Gram.		Gram.
5 c.c.	20·01 c.c.	0·028637	0·090884	0·090902
5 „	19·78 „	0·028015		
6 „	23·92 „	0·034232		
26·5 „	20·08 „	0·143682	0·430114	0·430184
26·5 „	19·95 „	0·143322		
26·5 „	20·00 „	0·143110		

Mercuric Sebate.—A solution containing 4 grams of this salt per litre (in hydrochloric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric sebate.	
		Found.	Used.
		Gram.	Gram.
25.c.c.	20·08 c.c.	0·10040	
25 „	20·10 „	0·10050 } 0·30065	0·3
25 „	19·95 „	0·09975	

Mercuric Citrate (Tribasic).—A solution containing 2·7284 grams of this salt per litre (in hydrochloric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric citrate.	
		Found.	Used.
		Gram.	Gram.
10 c.c.	8·25 c.c.	0·026572	
10 „	8·46 „	0·027611 } 0·081465	0·082152
10 „	8·38 „	0·027282	
25 „	21·03 „	0·069072	0·068660

Another solution of the same salt, containing 3·26 grams per litre, gave the following results:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric citrate.	
		Found.	Used.
		Gram.	Gram.
5 c.c.	5·06 c.c.	0·016495	
10 „	10·02 „	0·032730 } 6·098386	0·0978
15 „	15·08 „	0·049161	

Mercuric Cyanide.—A solution containing 2·18 grams of this salt per litre (in hydrochloric acid), was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric cyanide.		
		Found.		Used.
		Gram.		Gram.
5 c.c.	17·50 c.c.	0·011019	0·032729	0·0327
5 "	17·20 "	0·010830		
5 "	17·28 "	0·010880		
30 "	26·00 "	0·065500	0·131272	0·1308
30 "	26·10 "	0·065772		

The foregoing mercury compounds have also been estimated when mixed with different amounts of other substances, such as the nitrates, sulphates, oxalates, citrates, acetates, butyrates, chlorides, &c., of potassium, sodium, and (in different quantities) of the corresponding salts of calcium and magnesium.

Neither these substances, nor various organic bodies, interfere in any way with the applicability of the process.

It may be mentioned that the sixth decimal figure in the above statements of analytical results is valueless, except so far as it points out the variations of which the process admits; in other words its degree of accuracy. Fewer figures would not so well have shown the differences between the repetitions of the same analyses.

The results above recorded indicate very clearly—

1st. That Hannay's process may be safely applied to the estimation of mercury, not only in pure solutions of $HgCl_2$, but likewise in every salt of that metal.

2nd. That while the presence of ammoniacal salts radically interferes with the application of Hannay's method, still, if the precautions we suggest be carried out, the presence of such "foreign material" does not interfere with the trustworthiness of the results.

3rd. That, so far as we have yet gone, organic matters are of no moment.

This latter point, however, still remains to be investigated, when it is hoped that results will be obtained which will furnish us with a mode of rapidly and accurately estimating small quantities of mercury in chemico-physiological and chemico-toxicological inquiries.

XXXI.—*Note on the Discovery of Diamyl.*

By HARRY GRIMSHAW, F.C.S., late Demonstrator in the Laboratory of the Owen's College.

IN my paper read before this Society, and published in the September number of the Society's *Journal* (1877, ii, 260), the discovery of diamyl is, through an oversight, attributed to Wurtz (in 1855). The priority, however, rests with Dr. Frankland, who first prepared it (in 1851) by heating zinc-amalgam with amyl iodide in sealed tubes (*Chem. Soc. J.*, iii, 30). The resulting diamyl was found to boil at 155°, under a pressure of 728 mm., and had a sp. gr. of 0·7704 at 11°.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

The Spectra of Chemical Compounds. By J. MOSER (*Pogg. Ann.*, clx, 177—199).—The author proposes to discuss in this paper the question as to whether spectrum analysis may be taken as a means of direct qualitative analysis; he therefore asks the following questions:—

1. Is the spectrum of a compound equal to the sum of the spectra of its constituent elements?
2. Is it possible at once to determine from the spectrum of a compound what are its elements?
3. Or, has every chemical compound its own characteristic spectrum?

The first part of the paper consists of a discussion of the views of Kirchoff and Bunsen on the one hand, and on the other, of those investigators who have continued their researches. In observing emission spectra of the metals, Kirchoff and Bunsen were led to the conclusion that the spectra of metals were not influenced by the compounds which were volatilised to produce them; at the same time they added, that the volatilised salts were decomposed, and that therefore it was always the spectrum of the free metal which was obtained, and consequently it was possible that a chemical compound might show other lines than those of its elements. The proof that chemical compounds have their own spectra, the author does not consider has up to the present time been given. Those physicists who have asserted this fact, have rested their conclusions upon the observation of emission spectra, but by the observation of these alone, Kirchoff's objection cannot be answered; whereas the author, by the observation of absorption spectra, has shown that this method gives the required proof; answering at the same time all Kirchoff's objections. Kirchoff asserts that the differences observed in spectra of the same substance are due to changes of temperature alone, *e.g.*, in the case of Plücker and Hittorff's observations, the different spectra obtained from carbon compounds were all ascribed to the elementary carbon at different temperatures; whereas Ångström and Thalèn ascribe the different spectra mentioned by the former observers, to CN,CO,CO_2 and acetylene.

The question now arises, can the observation of absorption spectra be taken as being of equal value in the determination of chemical constitution, as that of emission spectra. This the author proves in a series of experiments upon both kinds of spectra in connection with the elements bromine and iodine; and the compound nitrous acid; the results of these experiments being given in a series of tables, for which the original paper must be consulted. From these he arrives at the following conclusions. The equal value of absorption spectra at a low, and of the other spectra at a high temperature, is proved by the similar characters of an absorption spectrum and of an emission spectrum at a low temperature, for the same chemical compound. Another proof is the appearance and disappearance of lines analogous to those first described by Kirchoff for emission spectra. Having shown the absorption spectra to be of equal value with emission spectra, for determining the question whether compounds have characteristic spectra, the next question comes to be, are there a sufficient number of observations, and are there no exceptions, so that we may be able to deduce a law. In answer to the first question, Moser calls attention to the large number of compounds investigated by Gernez in 1872 (gaseous compounds) of the metalloïds, and of Morton and Bolton in 1873 (absorption spectra of uranium salts).

But although numerous observations are at hand, their importance diminishes before that of the vast series of bodies such as the compounds of Ni.Co.Fe.Cr, and of the aniline, carbolic, naphthalene, anthracene and cinchonine colours, which show even to the naked eye the vast quantity of absorption phenomena already existing. The question whether the compounds of the same elements in different proportions give similar spectra, must also be answered in the negative, when the different colours of oxides and sesquioxides, of chlorous and chloric, of iodous and iodic compounds, and also of those organic colouring matters composed simply of C.H.O. and N. are remembered. In short, a series of observations as large as any from which a law of nature has ever been deduced are presented to us in this case.

A natural law, however, does not admit of any exceptions, and in these cases there are unfortunately two, the oxygen-compounds of nitrogen and chlorine. Of the first of these the trioxide and tetroxide of nitrogen show the same spectrum in their gaseous state. In a treatise to be published by the author, he has determined this point, and has at the same time tried to prove that the gaseous oxygen compound of nitrogen of a red brown colour is dissociated NO_2. Should he be able to prove this, the exception would be done away with, and there would remain only that of the oxygen-compounds of chlorine. W. A. Miller has already (1846) noticed the similarity of the spectra of chlorous acid, hypochlorous acid, and euchlorine; but as euchlorine is now acknowledged to be a mixture, it is probable that only one coloured compound is contained in these acids of chlorine. These single exceptions should also not be strictly dwelt upon, since the investigations of these bodies cannot be regarded as absolutely determined on account of their explosive nature, and the consequent difficulty in their treatment.

The author then says, if a retrospective view be taken of the conclusions drawn by Kirchoff and Bunsen on the one hand, and by Mitscherlich, Ångström, &c., on the other, we may add that a conclusion intermediate between these views has been arrived at, in which the more important changes of the spectra may be ascribed to difference of chemical composition, whilst the less important changes are due to alterations of mass and temperature. By this he does not wish to conclude that an element cannot possess different spectra; these, however, can be explained in the sense of the above hypothesis by assuming that the spectrum produced at a low temperature is that of the still existing molecules, while the one at the higher temperature is produced by the atoms.

In conclusion, the author calls attention to the advantages obtained in the examination of spectra by the absorption method over that of the emission method. When the electric spark passes through a chemical compound, the latter undergoes decomposition, but in most cases the amount of this decomposition cannot be accurately determined; and in the case of flame spectra the same holds good though not to so great an extent. A second objection to the emission spectra is that they alter with the temperature, and as it is not possible to regulate high temperatures nor even to determine them with accuracy, it becomes difficult to repeat and compare experiments. In the case of absorption spectra both these difficulties disappear.

A systematic investigation of the absorption spectra applied to the examination of chemical reactions in solutions and in gaseous mixtures, would allow of the determination, not only of final but also of intermediate results, and would be of great help in the development of chemistry, in the direction of its becoming the mechanics of atoms.

J. M. T.

Sensitiveness to Light of Various Salts of Silver. By M. CAREY LEA (*Amer. Jour. Sci.*, xiii, 369).—Paper was impregnated with soluble salts of acids capable of forming insoluble compounds with silver. The paper was then floated on the surface of silver nitrate. Some of the paper was also treated with gallotannic acid. The paper was then exposed to diffused light for seven to twelve seconds, and the image developed by pyrogallol, ammonium carbonate, and potassium bromide.

None of the substances examined gave strong images, with the exception of the platinocyanide and the arsenite. Tannin was not found to exert any beneficial action.

C. W. W.

The Heat of Combustion of the Explosive Mixture of Hydrogen and Oxygen in Closed Vessels. By CARL VON THAN (*Deut. Chem. Ges. Ber.*, x, 947—952).—This was determined by introducing a measured quantity of the gaseous mixture into the eprouvette of the Bunsen's ice-calorimeter, burning it, and measuring the quantity of heat produced. A number of precautions were taken to preserve the calorimeter from the warmth of the neighbourhood, &c. It was placed in a vessel filled with pure snow, or ice. The calorimeter itself was so constructed, that the capillary tube was all in one piece with the calorimeter itself, requiring thus no stopper, cock, &c. The mercury, as well as the water, was thoroughly boiled in the calorimeter itself. The protruding end of the capillary tube was fused on to a mercury-pump. With this arrangement, it was possible to estimate a pressure in the inside of the calorimeter to half a millimeter. The formation of the ice cylinder in the calorimeter took place in a vacuum, so that not the smallest quantity of air could be present in the inside of the apparatus. A gram-thermal unit indicated on the capillary tube about 8—9 mm. The gas-mixture was obtained by the electrolysis of 10 per cent. pure sulphuric acid, and was completely dried by phosphoric anhydride. The vessel in which the combustion took place was called the heat-eudiometer. It consisted of a glass-tube, closed at both ends with Geissler's capillary taps. At the upper end two fine platinum wires were fused through the glass, to conduct the electric spark. The volume was accurately determined by calibrating with mercury. After passing the mixed gas through, for from 2 to 4 hours, the upper tap was closed, and the whole left over night in a room facing north. Early before sunrise, the temperature was determined with an exactly corrected Geissler's normal thermometer, and the pressure with a Perreaul kathetometer. The lower tap was now closed with a wooden key, half a meter long. During the reading off, the apparatus was protected from the heat of the observer's body by two glass plates, placed one behind another. The heat-eudiometer was now placed in the calorimeter, and left there till the mercurial column remained stationary. The gas was then fired. The error of reading off consisted at the highest of 0·0001 of the whole value. The heat-eudiometer was now taken out of the calorimeter, and opened under freshly boiled mercury, whereby about 0·3—0·6 per cent. of the original gas always remained. This was pure explosive mixture, which had escaped the combustion by remaining in the capillaries of the taps. This gas was carefully measured. By the heat of combustion, or total energy of the explosive mixture in question, is meant *that amount of actual energy which is given out when the gas at* 0° *and* 760 *mm., is converted into liquid water at* 0°. In the measurement of the gaseous mixture small differences were unavoidable in the dispersion of the gas before the combustion, owing to the alteration of atmospheric pressure. That the results of the single observations might be comparable with each other, a small quantity of energy, d, was added in thermal units, to the quantity of heat directly observed in the calorimeter; d expresses the difference of the dispersion at the commencement from that of the defined initial condition. The value of d was calculated according to the following equation:—

$$d = \frac{C_{pk} - C_{vk}}{a} s(V - V_0),$$

where C_{pk} and C_{vk} represent the mean specific heat of the explosive gaseous mixture under constant pressure, a the coefficient of expansion, s the weight of the unit of volume of the gas, V the volume of heat-eudiometer at 0°, V_0 the normal volume of the mixture employed. A similar correction was necessary on account of the latent heat of the non-condensed aqueous vapour after the combustion, l, which also was reckoned into thermal units according to the formula:—

$$l = \frac{V_{\pi}}{p_0} s_1 v,$$

in which V represents the volume of the heat-eudiometer, p the tension of the saturated aqueous vapour at 0°, s_1 the weight of the unit of volume, v the heat of evaporation, and p_0 the pressure of an atmosphere. If the normal volume of the burnt gaseous mixture be called V_n, the directly observed gram-units c_1, and the total difference of energy of the unit-volume of the gaseous mixture, e_v, also in gram-degrees, then we have:—

$$e_v = \frac{c_1 + d + l}{V_n}$$

The value of the corrections $d + l$ in comparison with the directly observed heat-units c_1, did not amount in any of the experiments to 0·5 per cent. of the latter. The mean of the latter five of seven experiments is $e_v = 2{\cdot}02930$. The probable error of the result is therefore 0·0018, and this does not reach 0·001 of the whole value. *According to this, 1 c.c. of explosive gas at 0° and 760 mm. produces, on combustion in a closed vessel to liquid water, a quantity of heat equal to 2·0293 gram-degrees.* Andrews obtained results which give 2·02858 as the value of e_v, agreeing very nearly with von Than's result. Taking as a basis 1 as the atomic weight of hydrogen, and 15·96 that of oxygen (Stas), and the specific gravities of these gases determined by Regnault, the heat of combustion of the unit of weight of hydrogen from the above data will be—

$$e_{vh} = 33{\cdot}982 \text{ Than.}$$
$$e_{vh} = 33{\cdot}970 \text{ Andrews.}$$

If therefore a gram of hydrogen gas of 0° and 760 mm. be burnt in a closed vessel with the necessary quantity of oxygen, to form liquid water at 0°, the quantity of heat produced amounts to 33·982 gram-degrees. These numbers cannot, for the most part, be directly compared with those hitherto obtained, as these relate to the combustion in open vessels, with ordinary atmospheric pressure. With all the care adopted, small errors crept in, in the measuring of the gases. A check-experiment was made by another and new method, which is independent of all the influences mentioned. A heat-eudiometer was constructed, the capillary tap of which was so arranged that it could be opened or shut inside the Bunsen's ice-calorimeter. The heat-eudiometer was exactly fitted to a capillary tube, which projected from the calorimeter and ice-chest. At the extreme end of this capillary tube was a two-way tap fused on. One way of the tap led to the electrolytic gas-apparatus, the other was connected with a mercurial-pump, serving also as a manometer.

When the heat-eudiometer was pumped empty, and had been filled with the gaseous mixture, the pressure was so regulated that it exactly corresponded with 760 mm. The capillary-tap of the heat-eudiometer was now closed, the gas exploded, and the readings taken. Into the vacuous heat-eudiometer more mixture was now admitted, and exploded after pressure regulation. These operations were repeated till enough water was obtained to weigh exactly. Thus the initial condition was always normal, whilst the estimation of the burnt gas was simply reduced to a weighing of the water formed, and complete independence was gained of the temperature, pressure and volume. Only one observation was made by this method, on account of an accident intervening. This gave the heat of combustion of the unit of weight of hydrogen = 34·0409, which means a deviation from the other values of only 0·14 per cent. The author intends to apply his method to the estimation of the differential energies of the most important gases. W. S.

Heat of Solution of Chlorine, Bromine, and Iodine Compounds. By J. THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1017—1023).—The following table gives a systematic view of the heat of solution of various compounds of the metals which the author has published from time to time during the past four years. The numbers are calculated for a temperature of 18°, and the last column shows the number of molecules of water contained in hydrated compounds, which are hygroscopic, &c., as determined by analyses:—

Radicle.	Formula.	Mols. of water in solution.	Heat of solution.	Analysis.
Potassium	KCl	200	− 4440	—
	KBr	200	− 5080	—
	KI	200	− 5110	—
Sodium	$NaCl$	100	− 1180	—
	$NaBr$	200	− 190	—
	NaI	200	+ 1220	—
	$NaBr + 2H_2O$	300	− 4710	2·10 mols.
	$NaI + 2H_2O$	300	− 4010	2·04 „
Lithium	$LiCl$	230	+ 8440	—
Barium	$BaCl_2$	400	+ 2070	—
	$BaBr_2$	400	+ 4980	—
	$BaCl_2 + 2H_2O$	400	− 4930	1·98 „
	$BaBr_2 + 2H_2O$	400	− 4130	2·00 „
Strontium	$SrCl_2$	400	+ 11140	—
	$SrBr_2$	400	+ 16110	—
	$SrCl_2 + 6H_2O$	400	− 7500	6·00 „
	$SrBr_2 + 6H_2O$	400	− 7200	6·18 „
Calcium	$CaCl_2$	300	+ 17410	—
	$CaBr_2$	400	+ 24510	—
	CaI_2	400	+ 27690	—
	$CaCl_2 + 6H_2O$	400	− 4340	6·07 „
Magnesium	$MgCl_2$	800	+ 35920	—
	$MgCl_2 + 6H_2O$	400	+ 2950	6·11 „
Aluminium	Al_2Cl_6	2500	+153690	—
Zinc..........	$ZnCl_2$	300	+ 15630	—
	$ZnBr_2$	400	+ 15030	—
	ZnI_2	400	+ 11310	—
Cadmium	$CdCl_2$	400	+ 3010	—
	$CdBr_2$	400	+ 440	—
	CdI_2	400	— 960	—
	$CdCl_2 + 2H_2O$	400	+ 760	2·10 „
	$CdBr_2 + 4H_2O$	600	− 7290	4·06 „
Manganese	$MnCl_2$	350	+ 16010	—
	$MnCl_2 + 4H_2O$	400	+ 1540	3·88 „
Iron..........	Fe_2Cl_6	2000	+ 63360	—
	$FeCl_2$	350	+ 17900	—
	$FeCl_2 + 4H_2O$	400	+ 2750	—
Cobalt........	$CoCl_2$	400	+ 18340	—
	$CoCl_2 + 6H_2O$	400	− 2850	5·80 „

Radicle.	Formula.	Mols. of water in solution.	Heat of solution.	Analysis.
Nickel	$NiCl_2$	400	+ 19170	—
	$NiCl_2 + 6H_2O$	400	− 1160	6·02 mols.
Copper	$CuCl_2$	600	+ 11080	—
	$CuBr_2$	400	+ 8250	—
	$CuCl_2 + 2H_2O$	400	+ 4170	1·99 „
Lead	$PbCl_2$	1800	− 6800	—
	$PbBr_2$	2500	− 10040	—
Thallium	Tl_2Cl_2	9000	− 20200	—
Mercury	$HgCl_2$	300	− 3300	—
	$HgCl_4K_2 + H_2O$	600	− 16390	—
	$HgBr_4K_2$	660	− 9750	—
	HgI_4K_2	800	− 9810	—
Phosphorus	PCl_3	1600	+ 65140	—
Arsenic	$AsCl_3$	450	+ 17580	—
Antimony	$SbCl_3$	900	+ 8370	—
Gold	$AuCl_3$	900	+ 4450	—
	$AuBr_3$	2000	− 3760	—
	$AuCl_3 + 2H_2O$	600	− 1690	2·10 „
	$AuCl_4H + 3H_2O$	450	− 5850	3·65 „
	$AuBr_4H + 5H_2O$	1000	− 11400	5·28 „
Tin	$SnCl_2$	300	+ 350	—
	$SnCl_4$	300	+ 29920	—
	$SnCl_2 + 2H_2O$	200	− 5370	—
	$SnCl_4K_2 + H_2O$	600	− 13420	—
	$SnCl_6K_2$	800	− 3380	—
Titanium	$TiCl_4$	1600	+ 57870	—
Silicon	$SiCl_4$	3000	+ 69260	—
Palladium	$PdCl_4K_2$	800	− 13630	—
	$PdCl_6K_2$	—	− 15000	—
Platinum	$PtCl_4K_2$	600	− 12220	—
	$PtCl_4Am_2$	600	− 8480	—
	$PtBr_4K_2$	800	− 10630	—
	$PtCl_6K_2$	—	− 13760	—
	$PtBr_6K_2$	2000	− 12260	—
	$PtCl_6Na_2 + 6H_2O$	900	− 10630	5·98 „
	$PtBr_6Na_2 + 6H_2O$	800	− 8550	6·05 „
	$PtCl_6Na_2$	800	+ 8540	—
	$PtBr_6Na_2$	600	+ 9990	—
Hydrogen	HCl	300	+ 17310	—
	HBr	400	+ 19940	—
	HI	500	+ 19210	—
Ammonium	NH_4Cl	200	− 3880	—
	NH_4Br	200	− 4380	—
	NH_4I	200	− 3550	—
Hydroxylamine	NOH_4Cl	200	− 3650	—
Platodiamine	$PtN_4H_{12}Cl_2 + H_2O$	400	− 8760	—
Triethylsulphine	$SC_6H_{15}I$	267	− 5750	—

The anhydrous chlorides, bromides, and iodides dissolve in water with *either evolution or absorption of heat*, aluminium chloride showing the greatest evolution, and thallium chloride the greatest absorption.

The anhydrous chlorides, bromides, and iodides, which dissolve in water with evolution of heat, form crystalline compounds with water.—To this group belong the haloïd compounds of Li, Ba, Sr, Ca, Mg, Al, Zn, Mn, Fe, Co, Ni, Cu, Sn. The heat of solution of the anhydrous chloride and bromide of cadmium is positive, and both bodies combine with water; cadmium iodide, on the other hand, has a negative value, and this body does not combine with water at ordinary temperatures. The heat of solution of the anhydrous chloride of gold, $AuCl_3$, is positive; that of the bromide, $AuBr_3$, negative; the former combines with water to produce the compound $AuCl_3 + 2H_2O$; the latter forms no hydrate. Sodium iodide shows a positive value, and crystallises in combination with water; the value for the bromide is almost nil, and the hydrate is easily decomposed; that of the chloride is negative, and it combines with water at a very low temperature only.

The hydrated compounds of chlorine, bromine, and iodine, generally absorb heat on solution in water, but the following are exceptions: $MgCl_2 + 6H_2O$, $MnCl_2 + 4H_2O$, $FeCl_2 + 4H_2O$, $CdCl_2 + 2H_2O$ and $CnCl_2 + 2H_2O$. It is not unlikely that compounds of these bodies with a larger proportion of water are possible.

The heat of formation of hydrates is positive, the evolution of heat being due, partly to the latent heat of water, and partly to the affinity of the haloïd compound for water, and its value depends on the number of molecules of water taken up.

The magnitude of the heat of solution of the anhydrous haloïd compounds appears to be subject to several laws.—In the case of the metals of the alkaline earths, the heat of solution increases with the increasing atomic weight of the electro-negative constituent, the chloride evolving least, the iodide most heat. At the same time the heat of solution rises regularly from barium to magnesium, *i.e.*, with the decreasing atomic weight of the electro-positive constituent.

The group of the alkali-metals shows a similar behaviour; but potassium and probably thallium form compounds in which the value decreases with the electro-negative element, and this is probably connected with the fact that these two metals form no hydrated haloïd compound.

A comparison of the two groups gives interesting results, thus: the difference of the heat of solution

between $BaCl_2$ and $Tl_2Cl_2 = 22270$
$SrCl_3$ „ $K_2Cl_2 = 20020$
$CaCl_2$ „ $Na_2Cl_3 = 19770$
$MgCl_2$ „ $Li_2Cl_2 = 19040$.

The compounds of the formula, R_2Cl_6, also show that the heat of solution for equivalent quantities is greater in proportion as the atomic weight of the electro-positive constituent is less.

The heat of solution of the haloïd compounds of the heavy metals exhibits the reverse of the above cases; for the quantity is greatest for the chlorides, and least for the iodides.

G. T. A.

Heat of Formation of Chloric Acid. By JULIUS THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1026, 1027).—Berthelot has determined the heat of formation of chloric acid by reduction with sulphurous acid, and obtained results which agree very nearly with those published by the author (*J. pr. Chem.* [2], xi, 133).

$$ClO_3HAq, 3SO_2Aq = \begin{cases} 206320 & \text{Thomsen.} \\ 209700 & \text{Berthelot.} \end{cases}$$

Berthelot attributes the difference to his having used a weighed quantity of barium chlorate for his experiments, while Thomsen used a titrated solution of the acid; but this is not the reason, since the latter also used a weighed quantity of crystallised barium chlorate, but decomposed it by sulphuric acid previous to the experiments. They also arrive at slightly different results as to the heat of neutralisation of chloric acid.

$$BaAg, 2ClO_3HAq = \begin{cases} 28050 & \text{Thomsen.} \\ 27600 & \text{Berthelot.} \end{cases}$$

An error has also crept into Berthelot's paper with regard to hypochlorous acid, since Thomsen gives

$$\begin{aligned} Cl_2O &= -18040 \\ Cl_2OAq &= -\ 8600 \end{aligned}$$

while Berthelot's numbers are, – 15200 and – 5800. G. T. A.

Thermo-chemistry of the Substituted Anilines. By W. LOUGUININE (*Compt. rend.*, lxxxiv, 1227—1230).—This paper gives the measures of the heat disengaged when hydrochloric acid combines with ortho-, meta-, and para-chlorinated anilines, and with paranitraniline. The author draws the following conclusions from his experiments:—The heat disengaged in the combination of aniline bases is notably lessened when an atom of H is replaced by an electro-negative radicle. Para-toluidine disengages somewhat more heat than aniline, in combining with acids. The various isomeric modifications of monochloraniline do not liberate the same quantities of heat in combining with acids; the para-bases liberate the most heat, but the differences tend to disappear when the reactions are referred to the substances in the solid state. R. R.

Supersaturated Solutions. By D. GERNEZ (*Compt. rend.*, lxxxiv, 1389—1392). — When crystallisation is induced in supersaturated solutions, by rubbing with a solid body the sides of the vessel where in contact with the liquid, the crystals formed differ, in certain cases, in their degree of hydration, from those which the same liquid may deposit under other influences. Even the degree of intensity of the mechanical action may affect the result, as instanced by a supersaturated solution of calcium chloride, in which gentle friction induces the deposit of part of the salt in crystals containing $4H_2O$, while a second more vigorous rubbing determines the formation, in the remainder of the liquid, of crystals containing $6H_2O$. R. R.

Maintenance of Constant Temperatures. By A. D'ARSONVAL (*Compt. rend.*, lxxxiv, 456—458).—The arrangement devised by Bunsen for maintaining an enclosed space at a constant temperature consisted in surrounding the vessel with water or some other liquid heated by gas, the supply of the latter being regulated by the ascending column of a large mercurial thermometer dipping into the liquid. This arrangement has two defects:—1. The thermometer regulates the temperature for only a limited space around it; so that if the bath is very large, its various parts may be at very different temperatures. 2. The transmission of heat to the regulator is not immediate, and the best regulators on this principle cannot keep the temperature constant within a quarter of a degree.

The author's improvement consists in arranging two conical vessels concentrically, the inner one constituting the bath, which it is desired to maintain at a constant temperature. The space between them is completely filled with water, and is so arranged that as the water expands on heating, it presses against a caoutchouc membrane, which, being in connection with the gas supply, regulates the passage of the latter to the burner. By this arrangement both sources of error are eliminated, while the sensibility of the apparatus increases with its size. For a bath holding 20 litres of water, the expansion is about 3 to 4 c.c. for one degree; since $\frac{1}{50}$ c.c. suffices to regulate the supply, the temperature of the bath can be kept constant within $\frac{1}{100}$th of a degree.

J. W.

A Modification of Dumas' Method of Determining Vapour-densities. By J. HÄBERMANN (*Liebig's Annalen*, clxxxvii, 341—349),—The author applies to the process of Dumas the same modification that was applied by Hofmann to Gay-Lussac's process; that is, he determines vapour-densities under reduced pressure. This is effected by connecting the flask containing the substance of which the vapour-density is to be determined, with a water-pump furnished with a manometer, and exhausting to a pressure of about 500 mm. of mercury, whilst the flask is heated in an oil-bath to near the boiling point of the substance. The advantages claimed for the modified process are, that a vapour-density can be determined with less than 1 gram of substance, most of which is recoverable afterwards, and that the temperature need never exceed the boiling point of the substance. The paper gives details of manipulation, with a drawing of the apparatus, and several examples showing that the process works well.

J. R.

The Specific Gravity of Iodine Trichloride. A new Method of Determination for easily Decomposible Bodies. By A. C. CHRISTOMANOS (*Deut. Chem. Ges. Ber.*, x, 782—789).—The method described is one hit upon after many fruitless attempts to determine the specific gravity of iodine trichloride, and it appears to the author suitable in principle for the estimation of the specific gravity of many other volatile or easily decomposible or dissociated solid or liquid bodies. In the absence of a suitable apparatus furnished with glass taps, &c., the results so far were not so good as could be desired, but when this apparatus is ready, great confidence is expressed as to the correctness of the figures which will be obtained. The process in principle is as follows:—At a low temperature iodine trichloride remains unaltered in atmospheres of chlorine or of carbon dioxide. A glass vessel closed by glass taps is therefore filled with chlorine, and the weight of the vessel full of chlorine is taken. The chlorine is now driven out of the vessel by a stream of carbon dioxide, and the vessel is weighed again. The pure iodine trichloride is now introduced into the glass vessel, chlorine again passed through, and the vessel again weighed. The increase of the present weight is equal to that of the iodine trichloride less that of the portion of chlorine gas of equal bulk displaced by it. The weight of this volume of chlorine must now be found, in order to deduce from it directly the volume of the iodine trichloride, and indirectly its weight. The quotient from the two numbers gives the desired specific gravity. The chlorine gas over the iodine trichloride is then displaced by carbon dioxide in the cold, and the apparatus is again weighed. From this number the weight of the iodine trichloride is reckoned, less the weight of the equal bulk of carbon dioxide displaced. This volume of carbon dioxide is equal to that of the chlorine, and from the known specific gravity of these two gases a certain numerical relation may be deduced. By substituting this, the weight of the quantity of chlorine is obtained, and consequently its volume, and next the weight of an equal volume of water; lastly, the absolute weight of the iodine trichloride is deduced, and this without its being either actually weighed or measured.

W. S.

Volume Constitution of Solids. By H. SCHRÖDER (*Pogg. Ann.*, clx, 199—219).—This communication is a continuation of one published in the supplement to the above Journal, vi, 81—82, in which the author has described the isomorphous rhombic sulphates.

Isomorphous Rhombic Sulphates.—The author shows that in these the lead and strontium compounds must be considered as isosteric. From his observations it is shown that vol. Sr = Pb = K = 18·14; vol. Ba = NH_4 = Tl = 22·65; and vol. SO_4 = 29·45 nearly, these being in the simple relation 8 : 10 : 13. In the rhombic carbonates of similar crystalline form, vol. Ca = 11·33 = $\frac{1}{2}$ vol. Ba, and vol. CO_3 = 22·65 = vol. Ba. The metallic components Sr, Pb, K, and Ba have the same vols. as in the corresponding sulphates. The accuracy with which the volumes of the above-mentioned compounds have been determined shows that the simple relations of the component volumes are not to be ascribed to accident, but are the result of a natural law.

Rhombic Selenates and Chromates.—It has already been shown (*Liebig's Ann.* [1874], clxxii, 279) that the chromates and selenates are not only isomorphous, but isosteric, and from the fact that free rhombic WO_3 and CrO_3 are of equal volume and isoteric; the chromates and tungstates, so far as at present compared, are isosteric, but not isomorphous.

Volume-constitution of Oxygen in the above-mentioned Sulphates, Selenates, and Chromates.—Besides determining the volumes of the metallic radicles, it is necessary also to determine those of the acid radicles;

for this purpose the volume of oxygen is taken as 4·5—4·6, which is that found in periclase, magnetite, spinel, in which the volume of silica is the same as in quartz and the silicates. This reasoning has the advantage that the volumes of the acid radicles are in the simplest relation to those of the metallic radicles and the components of SO_4 and CrO_4.

General Volume-units.—From the above, it becomes obvious that all volumes can be brought to a common measure; this is possible only if the reasoning is guided by the following hypothesis—"All bodies combine in whole volumes." In the case of gaseous bodies this can be proved without exception by reducing to a common temperature and pressure. For liquids it has already been shown that the vols. of C, H_2, and O, in volatile organic liquids are equal in all compounds. if they are measured at proportional distances from the boiling-points. For solids the author hopes to prove the hypothesis. In fixing the measuring volume (maas-volum), or general volume unit, the guiding principle must be to choose as unit that which gives the simplest expressions, for instance, the smallest numbers for the expression of the elements and their compounds. After a full consideration of the various possible values of O taken as general volume unit, the author finally adopts O = 9, with the possible variation 8·6 to 9·6.

The Volume-unit in its relation to the variations of the General Volume-unit.—As already mentioned, the general volume-unit is variable in certain narrow limits with the nature of the bodies and their crystalline form. This variability seems to be due to the same causes as in the case of gases and liquids.

a. In the case of gaseous components, the general volume-unit depends on the temperature and pressure at which the gas is measured, and is nearly identical for all components.

b. The compressibility of liquids is small, but their expansion by heat is of considerable importance. The general volume-unit is therefore dependent on the temperature at which they are measured. They are best measured near the boiling-point.

c. As solid bodies remain *comparatively* unchanged by temperature and pressure, whole groups of bodies will give a practically constant general unit as long as their physical properties remain unchanged, as proved in the case of one isomorphous group.

Determination of the Molecule.—From the above the author thinks it becomes possible to fix the number of atoms in the molecule of a solid body; for if substances combine only in whole volumes, then the molecule of a body must contain the number of atoms which are necessary for the components and the elements of the compound, to fill the space of a whole number of volume-units. After giving several examples, the following objections are raised;—that the general volume-unit being variable when the volumes themselves are not accurately determined, several possible molecular formulæ might be assigned to the same group of bodies, or that the problem is not solved when both quantities are unknown. It is therefore possible to solve this problem only when one of the possible formulæ is shown to be very generally applicable, and at the same time gives a constant general volume-unit, agreeing with the crystalline form and composition of the body. This is the case in the spinel, garnet, amphibole, crysolite, and felspar groups, and also in the case of the carbonates, selenates, sulphates, and tungstates, chlorides, bromides, and some sulphides. These objections having been stated, the author does not deny that numerous observations are still required to answer them, but at the same time he thinks that this hypothesis is at all events an approximation to the truth, which will be useful as giving a foundation for future investigation and experiment, for the want of which the large number of carefully determined volumes of bodies have up to the present been practically useless. In conclusion, the author gives molecular formulæ for the spinels, garnets, and felspars. J. M. T.

Elasticity of Metals at different Temperatures. By G. PISALI (*Gazzetta chimica italiana*, vii, 173—188).—This paper contains the mathematical discussion of the results obtained by the author in his researches, abstracts of which have appeared in this *Journal* (1877, i, 38; ii, 162), including formulæ for modulus of torsion at various temperatures of each of the metals examined, both hard and annealed; the experimental results in all cases agreeing very closely with those calculated by means of the formula given. Also formulæ for the decrease in amplitude of successive oscillations, and tables comparing the calculated with the experimental numbers. The duration of an oscillation generally decreases with the amplitude, although the law is not always the same. Kupffer has proposed the expression

$$t_c = t\left(1 - kr\sqrt{\frac{a}{l}}\right),$$

where t is the duration and a the amplitude of the oscillation, r and l the radius and length of the wire, and k a constant independent of the dimensions of the wire, but varying with its chemical nature, its physical state (annealed or unannealed), and the temperature. This constant was called by Kupffer the "*coefficient of fluidity.*" Kupffer's formula, however, does not give satisfactory results according to the author, who finds that the decrease in duration of successive oscillations in wires reduced to the normal state, is in the greater number of cases very small, and in some quite insignificant.

The author also compares his results with those obtained by Kupffer, by Kohlrausch and Loomis, and by Streintz, and points out that the differences are in great part owing to the wires employed by these physicists not being in the normal elastic state: for Streintz, although he had accurately stated the tendency which metallic wires have to accommodate themselves to a definite state of elasticity, paid no attention to this in his experiments, almost all of which were made during periods of variable elasticity.

From the results of the author's experiments, it would appear that the elastic state of a wire within given limits of temperature presents two distinct periods; in the first the total number of oscillations and the modulus of torsion at a fixed temperature gradually increase, whilst the duration of successive oscillations varies in a somewhat irregular manner, and the wire, when it comes to rest, is permanently in a sensible state of torsion. On continuing the oscillations at various temperatures between the fixed limits, however, the wire gradually passes into a definite normal state for the given limits of temperature, in which these irregularities disappear. If the temperature be then raised higher than the former limit, the wire passes again into a variable state, which only becomes normal after long-continued oscillation. A change in the weight of the counterpoise, or a suppression of the tension for a short time, also alters the elastic state of the wire, which becomes normal only after frequent repetition of the changes in the conditions of experiment with long-continued oscillation. From this it will be seen that the determination of the constants which refer to elasticity of torsion of the first and second order and the law of Coulomb itself, should be made with wires in a normal elastic state. The application of this to instruments of precision in which the torsion of metallic wires is employed is self-evident.

Great theoretical interest attaches to the phenomena of elasticity of the second order (*elastische Nachwirking*), for if this force is really due to friction between the molecules of which bodies are composed, it must have some relation to the form of the molecules, and the study of the phenomena it produces may lead to a knowledge of a relation between the physico-mechanical structure and the chemical quantivalence of the elements. C. E. G.

Some Simple Laboratory Manipulations. By P. TOWSEND AUSTEN, (*Chem. News*, xxxvi, 49).—Felt pads are recommended to be placed under flasks and beakers, so as to prevent cracking by sudden cooling when placed on the laboratory table, and to avoid scratching by pieces of grit.

Microscopic crystals may easily be obtained, by placing on a warm watch glass a drop of the concentrated solution contained in a second watch glass, a thin film being thus obtained. The upper glass should not be pressed, but allowed to rest of itself. The drop thus expands into a film; and if a few drops of ether be placed in the upper watch glass, the cold resulting from its evaporation will cause crystallisation to take place between the two glasses. E. W. P.

Inorganic Chemistry.

New Mode of Manipulating Hydric Sulphide. By J. P. COOKE (*Amer. Jour. Sci.*, xiii, 427).—The author recommends the use of water saturated under pressure with hydric sulphide, both for qualitative and quantitative operations. The solution is prepared in a soda-water apparatus, of which drawings are given. Minute details of the preparation of the solution are given, but, without the woodcuts, they could not be clearly explained. C. W. W.

Preparation of Crystallised Phosphorous Acid. By H. GROS-

HEINTZ (*Bull. Soc. Chim.*, xxvii, 433).—Water cooled to 0° is saturated with phosphorus trichloride, the vapour of which is carried into the liquid by means of a current of dry air made to pass over the trichloride heated to 60°. The resulting mass of crystals is drained, washed with ice-cold water, and finally dried in a vacuum.

R. R.

Hypophosphoric Acid. By TH. SALZER (*Liebig's Annalen*, clxxxvii, 322—340).—The acid syrup formed when phosphorus, partially covered with water, is exposed to the air (Pelletier's *acide phosphatique*), contains phosphorous, phosphoric, and hypophosphoric acids. The last-named acid is produced by the action of the air on phosphorous acid. It may be separated in the form of a sparingly soluble sodium salt by treating the mixed acids with sodium carbonate or acetate.

Pure hypophosphoric acid is best obtained by treating the lead-salt suspended in water with hydrogen sulphide. Its aqueous solution is strongly acid, colourless, and inodorous, and may be boiled without decomposition, but when evaporated to a syrupy consistence, it is resolved by heat into phosphorous and phosphoric acids. In its behaviour with reagents, it is intermediate between phosphorous and phosphoric acids, which circumstance accounts for its having been so long overlooked in a mixture of these acids.

The acid is perfectly stable in aqueous solution, and is not affected by strong acids in the cold, but when boiled with dilute sulphuric or nitric acid, it is resolved, at a certain state of concentration, into phosphorous and phosphoric acids. The solution of the acid is not oxidised by dilute hydrogen peroxide when warmed therewith, and is not affected by potassium chromate, chlorine, or iodine, even at the boiling heat; neither does it reduce mercuric, auric, or platinic chloride. It produces in solutions of silver a white precipitate, which does not blacken on boiling. The solution is oxidised by potassium permanganate, slowly in the cold, and very rapidly when heated, being converted into phosphoric acid. It is not affected by hydrogen sulphide, sulphur trioxide, or nascent hydrogen.

Hypophosphoric acid is bibasic, and is represented by the formula, H_2PO_3, corresponding with the anhydride, P_2O_4.

The salts of hypophosphoric acid resemble in general those of hypophosphorous and phosphorous acids, being however, much more stable. At high temperatures they give off hydrogen or hydrogen phosphide, leaving metallic phosphide or phosphate.

The *acid sodium salt*, $NaHPO_3 + 3H_2O$, is formed on adding sodium acetate in excess to the syrupy liquid produced by the oxidation of moist phosphorus in the air. It crystallises in oblique rhombic prisms, which dissolve in 45 parts of cold, and 5 parts of boiling water. When gently warmed it loses its water of crystallisation, and afterwards gives off inflammable hydrogen, leaving metaphosphate. At ordinary temperatures, both the salt and its aqueous solution are perfectly stable.

The *neutral sodium salt*, $Na_2PO_3 + 5H_2O$, obtained by neutralising the acid salt with sodium carbonate, crystallises in needles, which dissolve in about 30 parts of cold water, forming a feebly alkaline solution.

The *lead salt*, $PbPO_3$, is precipitated by the acid sodium salt from a solution of neutral or basic acetate in the form of a white powder, insoluble in water, dilute acetic acid, and hypophosphoric acid, but soluble in dilute nitric acid. It is easily decomposed by dilute sulphuric acid. J. R.

Action of Ammonia on Sodium Phosphate. By J. S. DUNN (*Chem. News*, xxxvi, 88).—By adding strong ammonia to a cold saturated solution of sodium phosphate, a white crystalline slowly-subsiding precipitate is obtained, the amount of which varies with the proportions of ammonia and phosphate used. It begins to be formed when the proportion of ammonia to phosphate is about 1 to 2, and the maximum amount is obtained with about 3 volumes of ammonia to 2 of phosphate solution. The precipitate is readily soluble in water, but practically insoluble in strong ammonia. Analyses seem to show that its composition is not constant. D. B.

Some New Acid Ammonium Sulphates. By P. SCHWEITZER (*Chem. News*, xxxvi., 95—96).—In the course of an investigation into the methods of determining sulphuric acid, the author subjected ammonium sulphate to various degrees of heat, and noted the loss which it sustained by decomposition; certain regularities were thereby observed, which led him to determine the quantity of acid in the products obtained, and from these he deduces the existence of at least one new compound of ammonia and sulphuric acid.

1. *Ammonium Sulphate* $(NH_4)_2SO_4$.—The salt used was powdered and dried at 100°; it contained in 1·5081 grams 0·9177 gram SO_3, equal to 60·8514 per cent., theory requires 60·6061 per cent.

2. *Ammonium Bisulphate*, $NH_2.H.SO_4$.—The previous salt was heated until the thick pasty mass ceased to give off ammonia. On analysis, 1·7930 grams yielded 1·2403 grams SO_3, equal to 69·1746 per cent. It was then heated for 15 minutes longer, when it gave, on analysis in 1·9267 grams, 1·3390 grams SO_3, equal to 69·4971 per cent. No change having taken place in the composition of the substance by the second heating, the author infers the existence of a stable compound. Theoretically, the acid sulphate requires 69·5652 per cent.

3. *Biammonio-tetrahydric Sulphate* $(NH_4)_2H_4(SO_4)_3$.—The remainder of the previous salt was heated to a higher temperature until effervescence set in, and 3 grams had been lost. Analysis gave, in 1·2159 grams, 0·8818 gram SO_3, equal to 72·5224 per cent. The rest was heated a second time until another 3 grams had been volatilised, when the remainder gave, in 0·8637 gram, 0·6301 gram SO_3, equal to 72·9536 per cent. SO_3. This more acid ammonium sulphate, if constituted as above, requires 73·1717 per cent. SO_3. No trace of sulphurous acid was found in the salt. The reactions by which the two salts are obtained are probably these:—

1. $(NH_4)_2SO_4 = NH_4H.SO_4 + NH_3$
2. $4(NH_4H.SO_4) = (NH_4)_2H_4(SO_4)_3 + SO_2 + 2H_2O + N_2 + H_4.$

In conclusion, the author gives some figures showing the increase in weight of ammonium bisulphate placed under a bell-jar with a vessel containing water.
D. B.

Affinity of Metals for Sulphur and Oxygen. By OTTO SCHUMANN (*Liebig's Annalen*, clxxxvii, 286—321).—The author endeavours to arrive at the relative affinities of sulphur and oxygen for metals from a comparison of the results of experiments on the action (1) of hydrogen on sulphates, (2) of superheated steam on sulphides, and (3) of hydrogen sulphide on oxides. The substances experimented on were heated in tubes of glass or porcelain, while a current of pure hydrogen, or of steam, or hydrogen sulphide, was passed over them, and the products of the action were then analysed. The results arrived at are given in the following table, which shows, also, the results obtained in previous experiments by other investigators :—

Metal.	Action of hydrogen on the sulphate.	Action of steam on the sulphide.	Action of hydrogen sulphide on the oxide.
		Ia.	
Na	—	—	Na_2S (Kirscher).
K	K_2S (Berzelius).	—	—
		Ib.	
Cu	Cu (Arfvedson).	Cu (Regnault).	Cu_2S (Schumann).
Ag	Ag (Schumann).	Ag (Regnault) feeble.	Ag_2S (Böttger).
		IIa.	
Mg	MgO (?).	MgO (Schumann).	Very little MgS (Schumann).
Ca	CaS (Regnault).	CaO + very little $CaSO_4$ (Schumann).	4CaS + 3CaO (Schumann).
Sr	SrS (Forster). 12SrS + SrO (Schumann).	$SrSO_4$ (Schumann).	2SrS + SrO (Schumann).
Ba	BaS (Forster, Schumann).	$BaSO_4$ (Regnault, Lauth, Schumann).	BaS (Berzelius). 3BaS + BaO (Schumann).
		IIb.	
Zn	ZnOS (Arfvedson, Rammelsberg).	ZnO (Regnault).	ZnS (Arfvedson, Schumann).
Cd	CdS + Cd (Schüdler).	CdO (Regnault, Wackenroder).	CdS (Schumann).
Hg	Hg (Schumann).	Hg (Regnault)	HgS (Schumann).
		III.	
Al	Al_2O_3 (Schumann).	Al_2O_3 + a little $Al_2(SO_4)_3$ (Schumann).	A little Al_2S_3 (Schumann)

Metal.	Action of hydrogen on the sulphate.	Action of steam on the sulphide.	Action of hydrogen sulphide on the oxide.
IV.			
Ti	——	TiO_2 (Regnault).	——
Sn	Sn + SnS_2 (Arfvedson).	SnO_2 (Regnault).	SnS (from SnO) (Schumann). SnS_2 (from SnO_2).
Pb	Pb + PbS (Arfvedson, Rodwell).	PbS + Pb + PbO (Descotils). PbS + $PbSO_4$ (Pattinson).	Pb + PbS (Schumann).
V.			
As	——	As_2OS_2 (Regnault).	As_2S_2 (Schumann).
Sb	Sb_2O_3 + Sb + Sb_2S_3 (Arfvedson).	Sb_2OS_2 (Regnault).	$Sb_4O_2S_4$ (from Sb_2O_3). Sb_4OS_5 (from Sb_2O_5) (Schumann).
Bi	Bi (Arfvedson).	Bi (Regnault).	Bi_4S_3 (Schumann).
VI.			
Cr	Cr_2O_3 (Schrötter). Cr_2O_3 + Cr_2S_3 (Traube). $12Cr_2O_3$ + $Cr_4O_3S_3$ (Schumann).	Cr_2O_3 + Cr_2S_3 (Regnault).	Cr_2S_3 + Cr_2O_3 (Schumann).
VII.			
Mn	Mn_2OS (Arfvedson).	Mn_3O_4 (Regnault).	MnS (Arfvedson).
Fe	Fe_2S (from FeO). Fe_8S (from Fe_2O_3) (Arfvedson).	Fe_3O_4 (Regnault).	Fe_5S_6 (Rammelsberg). FeS (Sidot). FeS_2 (Berzelius).
Co	Co_2OS (Arfvedson).	CoO (Regnault).	Co_2OS (Schumann). Co_2S_3 (Berzelius). Co_4S_6 (Arfvedson). Co_4S_3 (Hjort).
Ni	Ni_2S (Arfvedson).	NiO (Regnault).	NiS (Arfvedson, Schumann).

In group I*a*, the experiments are incomplete, owing to the want of vessels which are not attacked by the fused sulphides. There can be little doubt, however, that the sulphides would be converted into sulphates, by the action of superheated steam; and since the oxides also yield sulphides with hydrogen sulphide, it follows that the metals of this group have a greater affinity for sulphur than for oxygen.

In group I*b*, copper and silver behave exactly alike, and the affinities of sulphur and oxygen for these metals are about equal.

In group II*a*, where the metals are arranged in the order of their atomic weights, the affinity for sulphur is seen to increase from magnesium to barium. Magnesium exhibits a greater affinity for oxygen; with calcium, the affinities for sulphur and for oxygen are about equal;

whilst strontium and barium display a decidedly greater affinity for sulphur.

In group II*b*, the affinities of the metals for sulphur and for oxygen are about equal. The action of hydrogen on the sulphates shows that the affinities of the metals for both metalloïds decrease in the order of the atomic weights, zinc yielding oxysulphide and cadmium yielding sulphide, whilst mercury yields only metal.

In group IV, the affinity of the metals is slightly greater for sulphur than for oxygen.

In group VII, manganese and iron exhibit equal affinities for sulphur and for oxygen. Nickel and cobalt show a somewhat greater affinity for sulphur.

The table exhibits a periodic rise and fall in the affinities of the metals for sulphur. In the first group the affinity decreases from potassium to silver. In the second group, it is almost *nil* with magnesium, increases from thence to barium, and decreases to mercury. In the third group, aluminium again shows a minimum of affinity for sulphur, which increases in the fourth and fifth groups to arsenic, and then decreases to bismuth. The affinity is once more at a minimum with chromium, and from thence increases throughout the seventh group.

The general conclusion from these experiments appears to be, that the strength of affinity for sulphur in relation to that for oxygen, is greatest in metals of highest atomic volume. J. R.

Solubility of Alkalis in Ether. By WILLIAM SKEY. (*Chem. News*, xxxvi, 48).—The alkalis dissolve in hydrous ether, as do also lime and magnesia. The alkalis and their carbonates appear, also, to dissolve in anhydrous ether, which likewise dissolves a notable quantity of the chlorides of calcium, nickel, zinc, cadmium, and platinum, as well as the thiocyanates of nickel, copper, and zinc: a small quantity of water added renders the ether turbid, due to the precipitation of these salts. E. W. P.

Action of Light and of Carbonic Acid on Potassium Iodide. By G. PELLAGRI (*Gazzetta chimica italiana*, vii, 297).—The author has made some experiments with the object of ascertaining the truth of Battandier's statement that the coloration of potassium iodide, when exposed to light, is due to the action of air and of carbonic acid, and finds that carbonic acid merely liberates hydriodic acid from solutions of potassium iodide, but that if the iodide is mixed with iodate, iodine is liberated, even if the solution is not exposed to light. Also, that potassium bicarbonate does not remove iodine, and that the action of light causes the liberation of iodine in solutions of potassium iodide and in ozonoscopic papers, without the intervention of carbonic acid or of ozone. C. E. G.

Preparation of Lithium, Cæsium, and Rubidium from Lepidolite. By H. PETERSON (*Dingl. polyt. J.*, ccxxiv, 176—179).—The mineral is strongly heated and thrown into cold water. The resulting powder is heated for a considerable time with sulphuric acid of 66° Beaumé; the filtered liquor is allowed to deposit crystals of cæsium and rubidium alum; the mother-liquor is treated with potash; the potassium alum is removed; and lithium is precipitated as carbonate by addition of sodium carbonate. The lithium carbonate is purified by causticising with lime, and the hydrate is reconverted into carbonate, which is now pure. The residue left after the first treatment with sulphuric acid, may be utilised for the manufacture of alum. M. M. P. M.

Magnesium, &c., in Zinc. By G. C. WITTSTEIN (*Dingl. polyt. J.*, ccxxiv, 208).—Metallic zinc very frequently contains small quantities of magnesium and aluminium. M. M. P. M.

Magnesium Fluoride. By A. COSSA (*Gazzetta chimica italiana*, vii, 212—219).—Almost the only notice about magnesium fluoride since the time of Berzelius is the discovery by Struever of a native crystalline magnesium fluoride, named *sellaite*, near Moutiers, in Savoy. This induced the author to endeavour to prepare anhydrous magnesium fluoride artificially. On adding a solution of an alkaline fluoride to one of magnesium sulphate, an amorphous gelatinous precipitate of magnesium fluoride is obtained which is difficult to wash. A better process is to treat pure magnesia with pure hydrofluoric acid, and remove the excess of the latter by heating the product to 100°. All attempts, however, to prepare the fluoride in the crystalline state directly, failed; but on strongly heating the amorphous fluoride obtained by the processes just mentioned, it fuses completely, and on cooling solidifies to a crystalline mass. Magnesium fluoride crystallised in plates was obtained by fusing a mixture of the amorphous fluoride with an alkaline chloride, and removing the latter by treatment with water when the mixture had become cold. The crystals obtained in this manner are twin, and when examined by polarised light exhibit the same characters as those from the fused magnesium chloride. They have been measured by Struever, who pronounces them to be identical with the native fluoride, sellaite. The crystals have a density of 2·856 at 12°, and their hardness is 6. After being submitted to the influence of an electric current from a Ruhmkorff's coil for a short time, and then gently heated, they become fluorescent in the same way that fluor-spar does, emitting a violet light. Sellaite itself exhibits a similar property, as do also other crystalline fluorides; but neither calcium nor magnesium fluoride in the amorphous state is capable of being rendered fluorescent.

Crystalline magnesium fluoride melts at a very high temperature. It is insoluble in acids with exception of concentrated sulphuric acid, which readily decomposes it. With calcium, barium, and strontium sulphates it forms readily fusible compounds of definite composition. Heated with aluminium sulphate, it yields aluminium fluoride. C. E. G.

Action of Alkaline Haloïds upon Ultramarine. By KARL HEUMANN (*Deut. Chem. Ges. Ber.*, x, 1345—1346).—Referring to the communication of Jul. Philipp on the action of metallic salts on ultramarine, the author states that he has been engaged in investigating the action of the alkaline chlorides, bromides, and iodides on the purified silver-ultramarine previously described by himself. By the action of these salts, either in solution or in a state of fusion, he has succeeded in obtaining ultramarines which contain potassium, sodium, or lithium, in place of the silver. They have a blue or green colour. C. B.

Experimental Researches on Natural Sulphides. By STAN. MEUNIER (*Compt. rend.*, lxxxiv, 638—640).—Many natural sulphides, such as galena, iron pyrites, copper pyrites, blende, cinnabar, antimony sulphide, and even sodium monosulphide, when placed in the solid state in solutions of gold chloride, mercury chloride, or silver nitrate, determine the reduction of the metal. The reaction is as follows:—

$$3PbS + 2AuCl_3 = 3PbCl_2 + Au_2 + S_3$$
$$PbS + 2AgNO_3 = Pb(NO_3)_2 + Ag_2 +$$

These facts may perhaps be capable of explaining the mineralogical associations so frequently met with in metalliferous veins.

Sea-water, according to Malaguti and Durocher, always contains silver. If this water were to pass by infiltration along a vein of galena, the whole of the silver would be precipitated and concentrated by the sulphide. It is known that native silver exists in many galenas, and it is reasonable to imagine that it may have been introduced in the manner above stated; moreover, the silver being in fine division, and under circumstances favourable for sulphuration, is very likely to pass subsequently to the state of sulphide, and uniting with the original lead sulphide, would give rise to what is known as argentiferous galena.

Again, since the precipitation of the metal is accompanied by the liberation of sulphur, this may account for the existence of galenas containing an excess of sulphur; in the majority of cases, however, this sulphur would probably not remain long uncombined, but would either unite with the precipitated metal or pass away by some process of oxidation. The association of gold with pyrites may be explained by the action of the same or similar influences. J. W.

Manganese Sulphide. By PH. DE CLERMONT (*Compt. rend.*, lxxxiv, 653—656).—When flesh-coloured manganese sulphide is heated either alone or with water to 250°, it remains unaltered, but when the temperature is raised to 305° in presence of a small quantity of water, the colour of the sulphide is changed to green. The pink sulphide becomes green when heated in sealed tubes to 220° with ammonia, with hydrogen sulphide, or with a mixture of potassium and ammonium sulphydrates; but with potassium sulphydrate alone under similar conditions the colour changes to violet.

By boiling manganese carbonate with ammonium sulphydrate, or by heating them together in closed tubes to 200°, the green sulphide is produced. If potassium sulphydrate is substituted for the ammonium salt, the pink sulphide only is obtained. The colour of the pink sulphide is also changed by heating it in a current of dry ammonia or carbonic anhydride.

It has been stated that the green sulphide is in reality an oxysulphide of manganese; the author's experiments, however, show that the alteration in colour is not attended with absorption of oxygen, and, further, that while the weight of the green compound when dried at 105°, first in a current of hydrogen, and afterwards in hydrogen sulphide, remains constant, the weight of the pink sulphide when similarly treated is diminished by 9 per cent. The author, therefore, regards the former compound as the anhydrous, and the latter as the hydrated sulphide. The relative solubility of the two sulphides in ammoniacal salts points to the same conclusion; nevertheless, all attempts to produce the rose-coloured from the green sulphide by direct hydration were unsuccessful. J. W.

Action of Phosphorus Pentachloride on Tungstic Anhydride. By NICHOLAE TECLU (*Liebig's Annalen*, clxxxvii, 255—260).—When these substances are heated to 170° in sealed tubes, in the proportions indicated by the following equation, the sole products of the reaction are tungsten hexchloride and phosphorus oxychloride—

$$WO_3 + 3PCl_5 = WCl_6 + 3POCl_3.$$

Tungsten hexchloride is easily soluble in phosphorus oxychloride. The crystals retain their metallic lustre for 36 hours or longer in water at ordinary temperatures. They melt at 189°. J. R.

Oxidation of Iron in a Gas Furnace. By A. TERREIL and DAUBRÉE (*Compt. rend.*, lxxxiv, 1398—1401).—Bars of iron after exposure for some days to the action of heated carbonic oxide and carbonic acid gases in a furnace (Siemens') at the Paris gas works, were found changed for about the depth of 7 millimeters into a black crystalline substance, which appeared on analysis to consist of ferrous oxide, together with magnetic oxide of iron. These bars form part of the regulating apparatus of the furnace, and they are oxidised constantly at about the rate of half a millimeter depth each day. A coating of terra-cotta several centimeters thick, with which they are covered, does not prevent the oxidising action. These facts show how readily gases permeate solid bodies like terra-cotta and crystalline ferrous oxide, and they may throw some light on such geological phenomena as the metamorphic transformation of great thicknesses of solid rocks. R. R.

Preparation of Chrome Iron and Analogous Compounds. By M. GERBER (*Bull. Soc. Chim.*, xxvii, 435).—The chromites of calcium, barium, magnesium, zinc, &c., Cr_2O_4M'', have been obtained by a new process, and examined by the author. His process consists in heating the anhydrous chloride of the metal with potassium bichromate, washing the mass with boiling water, and treating it with hydrochloric acid to remove uncombined oxide. R. R.

Chloride of Cobalt-ammonium. By J. S. MERRICK (*Chem. News*, xxxvi, 115).—No double salt of cobalt and ammonium is formed when a mixture of their chlorides is crystallised. W. R.

Certain Chemical Effects of Oxygenised Graphite and Platinum. By WILLIAM SKEY (*Chem. News*, xxxvi, 60).—Graphite and platinum, after exposure to air, liberate iodine from a weak solution of potassium iodide in dilute sulphuric acid. This property is removed by ignition or by washing with alkaline solutions, and is restored by a short exposure to air, or contact with nascent hydrogen, or by treatment with dilute nitric acid. Such graphite or platinum transforms metallic mercury into mercurous chloride when voltaically paired with it. Charcoal, silver, and gold have the same properties, but in a much less marked degree. The author inclines to the view that the action is produced by absorbed oxygen; it is also possible that nitric acid formed by the combination of this oxygen with the nitrogen of the air might produce the same effects, but this view is not so probable. W. R.

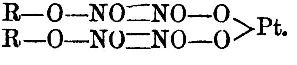
Action of Iodine and Alcohol on the Platino-nitrites. By L. F. NILSON (*Deut. Chem. Ges. Ber.*, x, 930—933).—During his researches on the platino-nitrites, the author, by treating the potassium and barium salts with iodine, obtained interesting iodine derivatives.

As the solutions of the above salts had a very slow action on the iodine, 1 mol. of the latter in alcoholic solution was therefore allowed to act on 1 mol. of the platino-nitrite. After spontaneous evaporation, small black crystals separated out from the dark, reddish-brown solution, probably an additive product analogous to the bromide observed by Blomstrand. On heating this solution, a violent evolution of gas occurred at 30—40°, during which aldehyde could easily be recognised by its odour. The solution cleared, and settled finally to a clear and beautiful amber-yellow. The potassium salt crystallised to a small extent on the edges of the vessel, forming a solid, black deposit; from this it was easy to free the iodo-derivative crystallising also from the solution, as the latter is very soluble in a little cold water, leaving behind the black substance, and crystallises readily from this solution. The *potassium salt* forms thus, after spontaneous evaporation of the solution, very large, four-sided, shining, amber-yellow prisms stable in the air, and losing water only when heated to 100°.

Analysis of the potassium salt led to the formula, $K_2.N_2O_4I_2.Pt + 2H_2O$.

The *barium salt*, $Ba.N_2O_4I_2.Pt + 4H_2O$, crystallises in beautiful, shining, amber-yellow, oblique, four-sided columns. It dissolves easily in water, remains unaltered in the air, and loses at 100° a part of its water.

Silver salt.—From the solution of the salts described, silver nitrate precipitates a completely amorphous compound, sparingly soluble in water, and of a lemon-yellow colour. Washed with water, and spread on filter paper, it assumes a blood-red colour, and the same change is observed after some time, in its faintly yellow solution. This change of colour depends probably on a molecular change, wherein silver iodide and some platino-nitrosic acids are formed, the latter compounds being distinguished by their characteristic red colour. This silver salt, when gently heated, first gives off red, and then violet vapours of nitrous acid and iodine respectively. The above salts were found to contain only half as much nitrogen as the platino-nitrites from which they are formed. The method of conversion is very remarkable. Doubtless the iodine simply adds itself to the platino-nitrite, and gives the iodide, $R_2.4NO_2.PtI_2$, wherein quadrivalent platinum is present. On raising the temperature, the alcohol takes part in the reaction. At 30—40° a change occurs; the platinum again becomes bivalent; while the two groups NO_2 escape, oxidising part of the alcohol to aldehyde, and forming ethyl nitrite, with another portion, and are replaced by the two iodine atoms. The constitution of the platino-nitrite is then expressed as follows :—



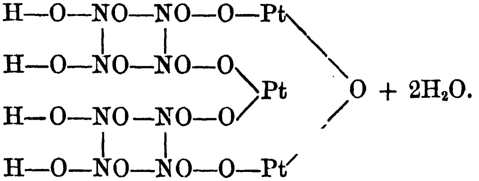
$$\left.\begin{array}{l}R-O-NO=NO-O\\R-O-NO=NO-O\end{array}\right>Pt.$$

and the iodine-compound will then be $\left.\begin{array}{l}R-O-NO\\R-O-NO\end{array}\right>Pt$, a very interesting middle-member between platino-nitrites and iodo-platinites. The formation from platino-nitrites, iodine, and alcohol is thus expressed :—

$$K_2.4NO_2.Pt + I_2 + 3C_2H_6O = R_2.N_2O_4I_2.Pt + C_2H_4O + 2[C_2H_5.O.NO] + 2H_2O.$$

That aldehyde can be formed without separation of platinum, shows with what great power the nitrogen and platinum are bound together. The radicle of the new salts is named *platino-di-iodo-dinitrosyl*, and the salts *platino-iodo-nitrites*. By double decomposition of the barium salt with sulphates, a whole series of these platino-isonitrites may doubtless be prepared, and with the investigation of these the author intends to proceed. W. S.

A new Platino-nitrosic Acid. By L. F. NILSON (*Deut. Chem. Ges. Ber.*, x, 934—936).—By decomposing a solution of barium platino-nitrite with an equivalent quantity of sulphuric acid, and evaporating in a vacuum over caustic potash, Lang obtained very fine, microscopic needles, resembling in colour chromic anhydride. These gave with water a yellow solution, which, when neutralised with potash, yielded a salt quite similar to the potassium platino-nitrite. This compound remained unaltered at 40—50°, became brown at 70—80°, and completely decomposed at higher temperatures. Lang regarded this compound as acid platinous nitrite, in consequence of the above properties, and because a sample dried over potassium carbonate gave on analysis 52·52 per cent. of platinum, that is to say, the quantity contained in the free acid of the platino-nitrite or platino-tetranitrosic acid, H_24NO_2Pt, which requires 51·29 per cent. of platinum. This question has been examined by the author. He finds that on decomposing barium platino-nitrite with sulphuric acid, even if no heat be employed, it is difficult to avoid loss of nitrous acid, the solution becoming blue. This difficulty is not removed even by evaporation in a vacuum, and a little air admitted into the bell-jar causes the immediate appearance of red fumes. Lang was not likely to observe this, as his absorbent (potash) would absorb the fumes as fast as they were formed. Lang's experiment was repeated, and the substance resembling chromic anhydride was obtained and analysed. The body was found to be easily soluble in water, forming a yellow, strongly acid solution. At 100° it gives off water alone, and no nitrogen. The numbers obtained led to the formula, $H_4.8NO_2.Pt_3O + 2H_2O$, in which platinum is contained to the extent of 58·35 per cent. The platino-tetranitrosic acid, which must accordingly be formed by the action of sulphuric acid on barium platino-nitrite, is very unstable. It gives up easily one-third of its nitrogen as nitrous acid, communicating the blue colour above-mentioned to the liquid, and passes into the new stable acid, which remains unaltered at 100°. This acid is remarkably constituted, for it can be considered as a compound of both the free acids which form the platino- and diplatino-nitrites. When saturated with potassium carbonate, however, it yields a homogeneous potassium salt, and cannot therefore be looked upon as a mixture of these acids in equal numbers of molecules, but as a veritable *triplatino-octonitrosic acid*, the constitution of which is expressed by the following formula:—



The following equation expresses the formation of this compound from the platino-tetranitrosic acid:—

$$3(H_2.4NO_2.Pt) = H_4.8NO_2.Pt_3O + 2(H.O.NO) + N_2O_3.$$

The potassium salt above alluded to crystallises in small, oblique, four-sided tables, rather soluble in warm water, but immediately crystallising out again on cooling. The crystals have a chrome-yellow colour, and mother-of-pearl lustre; they are stable in the air, and do not give off their water till heated to 100°. Analysis led to the formula,

$$K_4.8NO_2.Pt_3O + 2H_2O.$$

W. S.

Further Researches on Davyum. By SERGIUS KERN (*Chem. News*, xxxvi, 114).—The weight of the davyum ingot used in the author's investigations was 0·27 gram, which was dissolved in aqua regia. The following reactions were obtained with the solution of davyum chloride:—

Potash.—Light lemon-coloured precipitate, easily soluble in acids, giving a brownish mass of davyum nitrate, on evaporating its solution in nitric acid. The latter gives davyum monoxide on ignition. *Prussiate of potash* (yellow).—Brownish precipitate. *Potassium cyanide* yields a solution, giving on evaporation large prisms of cyanide of davyum and potassium. By passing hydrogen sulphide through a solution of the double salt, davyum-cyanic acid is obtained in the form of a crystalline red mass, which is decomposed even by a gentle heat. In acid davyum solutions hydrogen sulphide gives davyum sulphide, which dissolves in alkaline sulphides, probably yielding sulpho-salts.

From further experiments on the reaction of davyum chloride with soluble thiocyanates, the author finds that the red coloration thereby produced is due to the davyum itself, and not to the presence of iron or any other metal.

Davyum chloride is very soluble in water, alcohol, and ether. The carefully crystallised salt attracts moisture very slowly when heated before the blowpipe. It yields the monoxide, which is soluble in aqua regia. The chloride yields double salts with chloride of potassium, thallium, and ammonium. These are insoluble in water, but easily soluble in alcohol. The sodium salt is nearly insoluble in water and alcohol, a fact which is very interesting, as most of the sodium double salts of the metals of the platinum groups are very soluble in water. The chloride above mentioned is the only stable compound of chlorine and davyum. Davyum sulphate is obtained by leaving davyum for two hours in contact with boiling sulphuric acid. It forms a yellowish-red salt, nearly insoluble in water. The specific gravity of metallic davyum is as a mean, 9·389. Its atomic weight is not 100, as mentioned in a former paper, but near 154. The platinum ores do not contain more than 0·045 to 0·035 p. c. of davyum.

D. B.

Mineralogical Chemistry.

Association of Gold with Scheelite, in Idaho, U.S. By B. SILLIMAN (*Amer. Jour. Sci.*, xiii, 451).—The gold appears in the scheelite intimately associated with a small amount of pyrites, interspersed in the mass of scheelite and quartz. Chalcopyrite and leucopyrite are also present in small quantity.

The scheelite is massive, and of a yellow-brown colour. The density of the entire mass (scheelite, quartz, gold, &c.) is 3·27, which gives the proportion of quartz to scheelite as 2·46 : 1, disregarding the minor constituents. As the scheelite can easily be mechanically separated from the quartz, this may prove a valuable source of tungstic acid.

In Golden Queen Mine, Lake Co., Colorado, the gold occurs in minute crystalline granules in the scheelite, and fills what appears to have been a geode of scheelite crystals. C. W. W.

Barite Crystals from the Last Chance Mine, Morgan Co., Missouri; and Göthite, from Adair Co., Missouri. By G. C. BROADHEAD (*Amer. Jour. Sci.*, xiii, 419).—*Barite.*—The barite was found encrusting masses of limestone, sandstone, &c., either as separate crystals, or as a thin, transparent crust. The form of the crystals is different from that of any previously found in Missouri. They are elongated into prismatic forms ($\frac{1}{2}\bar{P}\infty$) in the direction of the macrodiagonal axis. The free extremity of the crystals is gradually sharpened off to a thin edge through the presence of a very low macrodome ($\frac{1}{8}\bar{P}\infty$). The central portion of all the crystals is perfectly transparent, and has a rhombic form corresponding with the fundamental (cleavage) plane; the rest of the crystals is opaque, milky white. A crystal from the Cordray mines has a rhombic form, the edges being bevelled by the planes, $\frac{1}{2}\bar{P}\infty$, which gave on measurement the angle 77° 40′.

Göthite.—Found in cavities in calcite concretions, in crystals from $\frac{1}{8}$ to $\frac{3}{4}$ inch long, aggregated in bundles, at the base of the calcite from which they radiate. Sometimes a single crystal will shoot directly through a calcite crystal. Sometimes also a quartz crystal will be seen penetrated in various directions with göthite. Minute, velvety balls of göthite, not larger than $\frac{1}{32}$ of an inch, were also found resting on the calcite. C. W. W.

Chemical Composition of Tryphyllite, from Grafton, New Hampshire. By S. L. PENFIELD (*Amer. Jour. Sci.*, xiii, 425).—Triphyllite is found at Grafton, imbedded in the granite in masses of varying size, and occasionally of 50 lbs. or more in weight. The exterior of the masses in some instances shows signs of decomposition, but a large portion of the material is fresh and undecomposed. It has a light blue colour, greasy to resinous lustre, and a perfect cleavage. Sp. gr. = 3·52. Analyses of the pure mineral, dried over sulphuric acid, show the following composition:—

P_2O_5.	FeO.	MnO.	CaO.	MgO.	Li_2O.	K_2O.	Na_2O.	H_2O.
44·18	26·09	18·17	0·89	0·56	8·77	0·32	0·16	1·47 = 100·61
43·88	26·38	18·24	0·99	0·61	8·81	0·32	0·09	1·47 = 100·79

leading to the formula, $10R_3PO_4 + 11R_3P_2O_8$. Water amounting to 0·50 per cent. was given off at 100°. C. W. W.

Examination of American Niobates or Columbates. By J. L. SMITH (*Amer. Jour. Sci.*, xiii, 361).—*Columbite from N. Carolina.*—Found in Mitchel Co., and Yancey Co., in rocks belonging to the same epoch as those in which samarskite was discovered. Occurs either in crystals, or in masses weighing from 5 to 100 grams. Sp. gr. of the crystals = 5·562; of the massive variety = 5·485. The following is the analysis of the two forms:—

	Massive.	Crystals.
Niobic (columbic) acid	80·82	80·06
Tungstic and stannic acids	1·02	1·21
Ferrous oxide	8·73	14·14
Manganous oxide	8·60	5·21
Cupric oxide	trace	—
	99·17	100·62

Columbite from Colorado.—Some crystals of amazon-stone from El Paso Co., were found to have small, black, acicular crystals imbedded beneath the surface. These latter were found to have the specific vity 5·15. Their composition is as follows:—Nb_2O_5 = 79·61, eO = 14·14, MnO = 4·61; loss by heat = 0·5.

Samarskite.—Occurs principally in a mica mine, Mitchel Co., N. Carolina. It is crystalline, black, brittle; fracture, conchoïdal; lustre, vitreous; hardness = 5·5 to 6. Sp. gr. = 5·72. Composition as follows:—

	(1)	(2)	(3)
Niobic acid	55·13	54·96	37·20
Tantalic acid	—		18·60
Tungstic and stannic acids	0·31	0·16	0·08
Yttria	14·49	12·84	14·45
Cerium oxides (?)	4·24	5·17	4·25
Uranium oxide	10·96	9·91	12·46
Manganous oxide	1·53	0·91	0·75
Ferrous oxide	11·74	14·02	10·90
Magnesia	trace	—	0·55 CaO
Loss on ignition	0·72	0·66	1·12
Insoluble residue	—	1·25	—
	99·12	99·88	100·36

Finkener and Stephans (*Verhand. Min. St. Pet.*, 1863, 13) found 4 p. c. zirconia and 6 p. c. thoria in this mineral.

Euxenite.—Found associated with samarskite, of a hair-brown colour, giving an ash-coloured powder, translucent in thin splinters. Fracture sub-conchoïdal and irregular; lustre resinoid. Sp. gr. (mean) = 4·608. No crystals were found. Analysis gave the following numbers:—

Nb_2O_5.	WO_3 and SnO_2.	Yttrium and cerium oxides.	CaO.	UO_3.	MnO.	FeO.	H_2O.
54·12	0·21	24·10	5·53	9·53	0·08	0·31	5·70 = 99·58

On *Hatchettolite* and *Rogersite*, see p. 576 of this volume.

Fergusonite.—Found in the granite quarries of Rockport, particularly at the intersection of two trap dykes.

The mineral is of a fine, dark brown colour, with a clear conchoïdal fracture, and resinous lustre. Hardness, 6; sp. gr. 5·681; streak, light brown; powder, ash-coloured. When heated to bright redness for 15 minutes, it changes to light greenish-yellow, with loss of 1·5 per cent. Nb_2O_5 = 48·75, Y_2O_3 = 46·01, CeO_2 = 4·23, Fe_2O_3, and UO_3 = 0·25, H_2O = 1·65.

The author concludes that the constitution of the principal niobium minerals is as follows:—Columbite is a simple niobate of iron and manganese; microlite is a calcium niobate; pyrochlore is a niobate of cerium and calcium; hatchettolite, neutral uranium and calcium niobate; samarskite, basic niobate of iron, uranium, and yttrium; yttrotantalite is basic yttrium and uranium niobate; euxenite the same, but hydrated; fergusonite is hydrated basic yttrium niobate.

C. W. W.

Chemical Examination of Turnerite. By F. Pisani (*Compt. rend.*, lxxxiv, 462—464).—A crystallographic examination of the *turnerite* of Binnenthal having led Trechmann to doubt the accuracy of the author's analysis of this mineral, the latter has re-examined the remaining portion of his original specimen, and has confirmed his previous statements. Having but 13½ milligrams at disposal, he was not able to do more than make approximate quantitative determinations. The results are, however, sufficiently accurate to show that turnerite consists essentially of cerium oxide combined with phosphoric acid, small quantities of lanthanum and didymium oxides also being present.

Phosphoric acid	28·4
Cerium oxide, lanthanum, &c.	68·0
	96·4

The approximate quantity of lanthanum oxide, extracted by dilute nitric acid, was 8·9 per cent.

The details of the analytical method are given in the original communication, together with some analyses of *monazite*, to which mineral turnerite appears to be closely related. J. W.

Composition of Lievrite as determined by Early's Method. By J. Emerson Reynolds (*Chem. News*, xxxvi, 85).—For the analysis of ferroso-ferric silicates the author recommends this method (*Chem. Soc. J.*, 1875, p, 286), which was used for analysing lievrite, a silicate easily acted upon by acids. As the formula of this mineral is by no means definitely fixed, the author requested Early to analyse by his method a portion of a particularly fine crystal obtained from the well-known Elba locality. The analysis was conducted in the following manner:—1·54 grams of the finely and recently powdered mineral were mixed with 20 c.c. of hydrofluoric acid (containing 20 p. c. of real acid), and the mixture boiled for five minutes in a deep platinum crucible; 10 c.c. of dilute (1 in 2) sulphuric acid were then added, and the boiling continued for a few minutes. The contents of the crucible were then washed into a flask with de-aërated water, and the amount of iron in the ferrous state determined as quickly as possible by a standard solution of potassium per manganate. Another quantity of the mineral was acted upon by strong hydrochloric acid; perfect decomposition was effected, and a gelatinous mass formed; the product was evaporated to dryness, and the silica separated in the usual way. The acid filtrate from the insoluble silica was then saturated with chlorine gas, and ammonia afterwards added in slight excess; the mixture was boiled in a closely covered beaker, to remove the excess of ammonia; the solution rapidly filtered; and the precipitate collected and ignited with the usual precautions, and weighed. The product contained all the iron as ferric oxide, alumina, manganese as Mn_3O_4, and a trace of silica. The latter was separated from the mixture by hydrochloric acid, and the filtrate subjected to the double treatment with pure caustic soda for the separation of alumina. The iron and manganese were then separated by the barium carbonate method. From the weight of iron thus found, that previously ascertained to be present in the ferrous state was deducted; the difference represented the weight of metal in the ferric state. The filtrate from the first precipitate caused by ammonia had the calcium separated from it as oxalate, and the latter was determined in the usual way. The filtrate from the calcium precipitate was then evaporated to dryness, and the residue heated to expel ammoniacal salts; the product of this treatment was dissolved with the aid of a few drops of hydrochloric acid, the magnesium separated by means of barium, hydrate and estimated; while the alkalis in the filtrate were converted into chlorides and weighed, and the potassium separated by platinic chloride. No trace of lithium was detected in the mineral. The water was estimated by heating a quantity of the freshly-powdered and unaltered mineral to redness in a hard glass tube, connected with a weighed chloride of calcium tube, obtained 0·422 p. c. The following is the percentage composition of the specimen analysed by Early:—

SiO_2.	FeO.	Fe_2O_3.	MnO.	CaO.	MgO.	Al_2O_3.	K_2O.	Na_2O.	H_2O.
29·93	31·83	20·16	3·02	13·71	0·30	0·36	0·20	0·29	0·42 = 100·22 p.c.

These data when dismissed in the usual way, give the following ratios:—

$$\left.\begin{array}{l} SiO_2 = 0{\cdot}4983 = 3{\cdot}85 = 4{\cdot}00 \\ RO \;\;= 0{\cdot}7431 = 5{\cdot}74 = 5{\cdot}96 \\ R_3O_2 = 0{\cdot}1294 = 1{\cdot}00 = 1{\cdot}04 \end{array}\right\} R_2O_3,6RO,4SiO_2;$$

where $6RO = 4(Fe,Mn)O + 2CaO$ nearly, neglecting the small amount of alkalis. As the water present in the particularly pure specimen of the mineral analysed did not reach 0·5 p.c., the author regards lievrite as an anhydrous silicate. The above analysis agrees in all essential points with those of Rammelsberg and Von Kobell. A comparison of various analyses of different specimens proves that there is little variation in the proportion of Fe^{vi}_2 to Fe''_4. The author is, therefore, disposed to regard the former as an essential constituent of the mineral rather than as a product of the oxidation of a calcio-ferrous silicate. D. B.

The Crystallisation of the Diamond. By A. SADEBECK (*Jahrb. f. Min.*, 1877, 197—199).—The author considers the holohedry of the diamond to be undoubted. He observed all the seven forms in the regular system, with the exception of the trapezohedron; but great difficulty was experienced in obtaining accurate measurements, owing to the convexity of the faces. The following forms were observed: $3O\frac{3}{2}$, $6O\frac{6}{5}$, $5O\frac{5}{4}$, $\infty O\frac{4}{3}$, $\infty O\frac{4}{10}$, $\infty O\frac{3}{3}$, $\infty O2$, $\infty O3$, $2O$. Simple tetrahedrons are unknown. The hemihedry observed on the diamond is only a form-development, as crystals of this mineral have been observed in South Africa exhibiting holohedry at one pole and hemihedry at the other. The twin growth of some diamonds is peculiar; for instance, the juxtaposition twins from Brazil (in which the octohedron predominates, and the crystals are curtailed in the direction of the twin axis) have the appearance of small triangular plates. Twin rhombic dodecahedrons and cubes are also common. G. Rose, who worked upon this subject, was of opinion that the diamond exhibited another twin-law besides the ordinary one, viz., "the twin axis a prismatic axis," a law which could be applicable only to hemihedral forms. His reason for assuming this law to be applicable to the diamond was the occurrence of forms closely resembling "penetration-twin" tetrahedrons and occasional octohedrons, with indented edges. Sadebeck examined the identical collection of diamonds which Rose had previously described, and perceived that the latter had mistaken indentations in the edges of the various crystals caused by a shell-like structure, for twin re-entering angles. The octohedron faces must be considered as the chief tectonic planes, and their prismatic axes as axes of the chief tectonic zones. C. A. B.

Enstatite Crystals from Kjörrestad, near Bamle, Norway.

By W. C. Brögger and G. vom Rath (*Jahrb. f. Min.*, 1877, 199—201).—Before the spring of 1874, well-developed attached crystals of enstatite were unknown in plutonic rocks, but the authors were fortunate in discovering them in a normal apatite-vein penetrating the mica and hornblende-slate at Hankedalsvand in the apatite mine of Kjörrestad, between Krageroe and Langesund. A large isolated mass, consisting almost entirely of enstatite and rutile (with only a trace of apatite), was found at the above locality, the enstatite crystals sometimes attaining a length of 38 cm., a breadth of 26 cm., and a thickness of 13 cm. One crystal was 40 cm. in length, but broken off at both ends. The crystals are enveloped in white or greenish talc, and are prismatic, being a combination of the primary prism with a strongly-developed macro-pinacoïd and a narrow brachy pinacoïd; but a great variety of distortions occur, the brachy-axis in some cases having the appearance of a clino-axis: others again possess a true rhombic character, and closely resemble the enstatite of Breitenbach, the hypersthene from the Rocher du Capuzin in the Montdore and from Laach. The primary pyramid of enstatite from Breitenbach and hypersthene from Laach furnished the following interfacial measurements:—

	Enstatite from Breitenbach.	Hypersthene from Laach.
Macrodiagonal edge	125° 52′	125° 58½′
Brachydiagonal edge....	127° 36′	127° 38½′
Lateral edge	78° 42′	78° 34½′

whence $a : b : c = 0{\cdot}97016 : 1 : 0{\cdot}57097$.

Only the cleavage angle (prism) of the Kjörrestad crystals could be measured by the reflecting goniometer, and was found to vary from 91° 25′ to 91° 40′, a measurement closely agreeing with the corresponding angles of enstatite from Breitenbach (91° 44′) and hypersthene from Laach (91° 44′). The following forms were observed in combinations on lenstatite from Kjörrestad, viz.: $\infty P \,.\, \infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, 0P \,.\, P2 \,.\, \tfrac{2}{3}P\infty \,.\, \tfrac{4}{3}\breve{P}\tfrac{4}{3} \,.\, \tfrac{1}{6}\breve{P}\infty \,.\, \tfrac{2}{7}\breve{P}\infty$ and $\tfrac{1}{2}\breve{P}\infty$; the last four being new.

Kjörrestad enstatite generally has a steatitic outer surface, a complete prismatic clearage, and an incomplete brachy diagonal cleavage. Sp. gr. 3·153. According to Descloiseaux, the optical axes lie in the brachy pinacoïd, the acute positive bisectrix being parallel to the edge of the vertical prism. Chemical composition as follows, viz.:—

SiO_2.	Al_2O_3.	FeO.	MgO.	H_2O.	
58·00	1·35	3·16	36·91	0·80	= 100·22

C. A. B.

Bastite from Elba. By F. PISANI (*Jahrb. f. Min.*, 1877, 203).—The specimen examined by the author came from La Venella, Circondario da Rio, Elba. It was easily cleavable into laminæ, possessing a metallic lustre, H. 3·5. Spec. gr. 2·59; leek-green to olive-green colour. A section made parallel to the basal terminal plane, examined in polarized light under the microscope, showed it to have an acute negative bisectrix normal to the cleavage plane, and proved the crystal-system to be rhombic; fused with difficulty before the blowpipe. Heated in the mattrass, it evolved water and was soluble in concentrated hydrochloric acid. Chemical composition as follows:—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	H_2O.	
39·10	3·61	8·03	33·60	3·28	12·60	= 100·22

C. A. B.

The Occurrence of Durangite in the Tin-ore District of Durango, Mexico. By H. HANKS (*Jahrb. f. Min.*, 1877, 203).—This mineral is found in the Barranca tin-mine, 18 miles N.W. of Coneto, Durango State, in a peculiar decomposed mass of gangue, occasionally accompanied by fine topazes. The best crystals of durangite are found "attached" on the sides of the tin-vein, and have an orange-yellow colour. The largest yet found weighs 3·022 grams, and has a length of 19 mm., and a breadth of 11 mm. C. A. B.

Gmelinite from Nova Scotia. By A. B. HOWE (*Jahrb. f. Min.* 1877, 201).—This mineral occurs in two distinct types in Nova Scotia, the first type, occurring at Two Islands and Cape Blomidon, exhibits + R and — R almost in equilibrium with ∞ R, OP, and ∞ P2. The prism ∞ R is horizontally striated; ∞ P2 has somewhat rounded edges, and the colour is light flesh-red to milk-white. The second type occurs on the Five Islands, eight miles distant from Two Islands. On this type there is an entire absence of OP; — R is scarcely discernible, ∞ R exhibits a strong lustre on its faces without a trace of striation. The characteristic form of this locality is — 2R, which is distinctly striated parallel to its combination edges with R, the crystals being complete rhombohedrons, some faces being well developed; other crystals, again, when small, exhibit drusy faces. Colour darker than in the crystals of the first type. Gmelinite from Bergen Hill occurs in a type intermediate between the two already described as R and — R, are unequally developed, and OR and ∞ P2 are not present. Chemical composition as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.
Two Islands..	51·36	17·81	0·15	5·68	3·92	0·23	20·96=100·11
Five Islands..	50·40	18·27	0·17	1·12	9·79	0·20	20·71=100·66
Bergen Hill..	48·67	18·72	0·10	2·60	9·14	—	21·35=100·58

From the above analysis it is evident that the chemical composition exerts a considerable influence upon the crystallographical type. Gmelinite from Five Islands contains a high amount of Na_2O, and has a rhombohedral type, R predominating, that from Bergen Hill exhibits no particular characteristics, whilst that from Two Islands, in which there is a high amount of CaO, is remarkable for its pyramidal "habit." C. A. B.

Goldsmith's Hexagonite, a Variety of Tremolite. By G. KOENIG (*Jahrb. f. Min.*, 1877, 202).—Goldsmith described a mineral from Edwards, St. Lawrence county, N.Y., under the name hexagonite, and assigned it a place amongst the beryl group. Having re-examined a large quantity of this mineral, the author found it to crystallise in the monosymmetrical system, the form being $0P \,.\, \infty P$, and the type tabular through OP. The prism angle 124° 39′ agrees closely with that of tremolite, viz., 124° 30′. Cleavage prismatic and incomplete, parallel to OP H 6·5. Spec. grav. 2·996. White or violet. Strong vitreous lustre. Fuses with difficultly before the blowpipe to a white enamel. Gives the reaction for manganese in the borax bead. Chemical composition as follows:—

SiO_2.	MgO.	CaO.	Na_2O.	MnO.	Al_2O_3—Fe_2O_3.		
58·20	24·14	12·20	1·90	1·37	1·40	=	99·21

C. A. B.

The Colouring Matter of Amazonstone from Pike's Peak, Colorado. By G. KOENIG (*Jahrb. f. Min.*, 1877, 202).—The author concludes that the base of the colouring matter is iron, probably combined with an organic acid. It could not be combined molecularly with the felspar, as in that case the hydrochloric acid could not dissolve out the iron after oxidation; it is therefore highly probable that the colouring matter was distributed throughout the mineral by infiltration through the numerous fine capillary hollows which it contained. C. A. B.

Zircon in the Amazonstone of Pike's Peak, Colorado. By G. KOENIG (*Jahrb. f. Min.*, 1877, 203).—Found in the form $P \,.\, \infty P \infty$, a quarter of an inch in length and an eighth of an inch in breadth, generally accompanied by acicular columbite. C. A. B.

Tridymite from the Hargittastock, Siebenbürgen. By C. DOELTER (*Jahrb. f. Min.*, 1877, 204—205).—Crystals from this neighbourhood sometimes attain a length of 1·5 mm., and are generally cloudy and of a reddish-brown or yellow colour; seldom transparent or colourless. Single crystals are rare, but the usual twin-formations common. All the forms observed by vom Rath on Mexican tridymite were also present on the specimens from Siebenbürgen. A microscopical examination revealed the presence of plagioclase, orthoclase, hornblende or augite laminæ, undeterminable microlites, and as a rarity isolated grains of magnetite. The author considers the rock in which this tridymite occurs to be andesite. C. A. B.

The Crystalline Rocks of Minnesota, U.S.A. (conclusion). By A. STRENG and J. H. KLOOS (*Jahrb. f. Min.*, 1877, 113—138, and 225—242).—*Hornblende-Gabbro.*—This rock is found only on the St. Louis river, near Duluth. In outward appearance it closely resembles a coarse-grained hypersthene rock, and consists of predominating plagioclase (labradorite), a little orthoclase, hornblende, diallagite, pegmatite, titanite, apatite, and extremely small quantities of copper-pyrites and epiodote, together with a little quartz. The hornblende is mostly of a light or dark-green colour, owing to the presence of viridite; sometimes it is of a brown colour, and penetrated by fine dark parallel systems of lines, but a remarkable feature of this brown variety is the entire absence of "cleavage-cracks." The apatite occurs in thick short crystals. An analysis of this rock showed it to have the following composition, viz.:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	
49·15	21·90	6·60	4·54	8·22	3·03	1·61	3·83	1·92	= 100·80

Augite Diorite.—This rock is found on the Sauk river near Richmond, and on the Mississippi, near Little Falls, above Watab. Macroscopically it appears to be a coarse-grained mixture of apparently predominating hornblende and greyish-white asymmetrical felspar, accompanied by an augitic mineral, biotite, iron-pyrites, and probably zircon. Microscopical examination proves it to be a mixture of plagioclase, hornblende, diallagite, biotite, a little iron-pyrites and magnetite, an extremely small quantity of quartz, apatite, and probably an occasional zircon crystal here and there. An analysis made of this rock furnished the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	
48·87	18·72	3·28	5·55	11·93	9·53	0·73	2·10	0·93	trace	= 101·64

P_2O_5 = 0·08, from which it appears to be a normal augitic rock. The high percentage of calcium oxide and magnesia point to a richness in plagioclase, hornblende and diallagite, whilst the small quantity of oxides of iron equally determine the absence of magnetite. From the small quantity of potash found, it is evident that orthoclase is almost altogether absent.

Augite Diorite from Bäremans Farm, near Richmond.—Differs from the last-mentioned specimen only in the absence of large hornblende crystals, the occurrence of larger felspar crystals, and the greater amounts of magnetite and apatite. Its composition is as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	
52·00	15·75	3·55	12·84	7·39	3·42	1·24	3·37	0·35	0·11	=100·02

P_2O_5 = 1·06, therefore (chemically speaking) this specimen differs from the first-mentioned augite-diorite in having orthoclase and a higher amount of magnetite and apatite present in its composition.

Augite Diorite (a) from Little Falls.—This specimen consists of a mixture of basic plagioclase with a large quantity of hornblende, occurring in groups of large crystals (many of which are twins), some diallagite and large isolated crystals of apatite, with a very small quantity of quartz and biotite. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	
46·52	13·87	3·71	8·79	11·00	10·04	1·01	2·13	1·05	0·47	=98·59

P_2O_5 = 0·32.

Augite Diorite (b) from Little Falls.—Differs from the last-mentioned specimen only in the larger quantity of quartz masses observed interspersed between the crystals of felspar. Chemical composition as follows :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	
52·35	15·72	2·90	7·32	8·98	7·36	1·32	2·81	1·35	0·23	=100·34

P_2O_5 = 0·30.

There was a trace of lithia observed.

Augite Diorite (c) from Little Falls.—Differs from *a* and *b* in the large quantity of diallagite present.

Augite Diorite (d) from Little Falls.—Is rich in plagioclase, otherwise there is not much difference between this and the preceding specimens. Chemical composition as follows :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	
51·27	23·72	1·35	3·81	10·50	3·30	0·65	3·35	1·23	0·35	= 99·53

P_2O_5 = 0·37.

Contains a trace of lithia.

The authors conclude from their examination of the augite diorite of the Richmond district, that it consists in general of a mixture of basic plagioclase closely allied to labradorite, with hornblende intimately associated with diallagite, biotite, magnetite, apatite and extremely small quantities of quartz, and possibly titanite. It resembles hornblende-gabbro in constitution, but does not contain so much augite as that rock, and differs from it in the smaller amounts of magnetite and titanite present. Minute descriptions are given throughout of the microscopical appearances of the constituents of the various rocks under examination.

QUARTZOSE DIORITE.—*Quartzose Diorite from Sauk Centre.*—Macroscopically examined proved to be a mixture of greyish-white felspar, quartz in irregular grey-coloured grains, hornblende of a dark brownish-black colour, titanite, iron-pyrites and epidote. Microscopically examined, it was observed that the predominating felspar was asymmetrical (triclinic), associated with a little orthoclase, and enclosing green grains of a substance resembling viridite. The hornblende sometimes occurred in radia-fibrous, or interwoven aggregates, penetrated with a viridite-like substance. Apatite was found in needles sometimes 0·2 mm. in length, and 0·07 mm. in thickness; also in hexagonal sections. Chemical composition as follows :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	
56·59	12·41	5·39	10·28	6·70	2·02	1·02	4·27	1·45	trace	= 100·13

P_2O_5 0 14.
TiO_2 0·22.

Quartzose Diorite from Little Falls.—This specimen differed macroscopically from the last-mentioned one, in the very distinct well-defined black hornblende crystals which were observed in it, the presence of well-developed garnet crystals and the entire absence of titanite. Its chemical composition was as follows :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO,	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	P_2O.	
66·88	11·69	1·68	8·94	5·45	3·55	0·20	1·25	1·03	trace	trace	= 100·67

A striking feature of this specimen is the high percentage of silica and the low percentage of alumina, thus showing that it is rich in quartz, but poor in felspar. Quartzose diorite from Little Falls is a mixture of large hornblende crystals embedded in a fine-grained aggregate of quartz, plagioclase, black grains of unknown composition, biotite in small quantity, and garnets. The authors consider the independent character of this rock to be doubtful.

AUGITE-QUARTZOSE DIORITE.—*Augite-quartzose Diorite (a) from Watab.*—Appears macroscopically to be a granular mixture of lustrous asymmetrical felspar, reddish fresh orthoclase, irregular quartz grains, biotite and greenish-black, strongly lustrous hornblende, which is not in such quantity as the felspar. In the interior of the large hornblende crystals there is a kernel of diallagite. Examined under the microscope this specimen exhibits numerous fluid enclosures and apatite needles in the quartz substance, whilst the diallagite is of a light yellowish-green colour, penetrated by biotite laminæ or greenish-viridite grains; also traces of titanite and magnetite. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	
65·27	15·76	1·36	3·44	3·70	2·14	3·97	4·57	0·42	= 100·63

P_2O_5 = 0·26.

It is evident that this rock is still fresh, and closely approaches a typical syenite in composition, particularly the syenite granite of Watab, but it differs from the latter in the distinct presence of diallagite. The high percentage of quartz proves it to be a different rock to the augite-diorites, and the amount of orthoclase and diallagite present show it to be perfectly distinct from the quartzose diorites; hence it may be named with propriety augite-quartzose diorite.

Augite-quartzose Diorite (b) from Watab.—Differs only slightly macroscopically from the last-named specimen, being a coarse-grained mixture of reddish orthoclase, white or greyish plagioclase (asymmetrical felspar), black hornblende, diallagite, biotite, magnetite, and titanite grains in great numbers, iron pyrites, and numerous large apatite needles. Its microscopical appearance resembles the specimen (*a*), and requires no further description.

SYENITE-GRANITE (HORNBLENDE-GRANITE).—*Syenite-granite (a) from Sauk Rapids.*—Is a moderately coarse-grained mixture of reddish orthoclase, oligoclase, and quartz, with smaller amounts of hornblende, biotite, magnetite, apatite, and here and there isolated, greenish-brown, pyramidal crystals, which could not be further determined. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	P_2O_5.
67·70	16·11	2·47	2·29	2·89	1·11	4·47	3·64	0·83	trace	0·13

= 101·64

Syenite-granite (b) from Sauk Rapids.—Differs only slightly from the last-mentioned specimen in the hornblende aggregates being more decomposed.

Syenite-granite from St. Cloud.—Consists macroscopically of a mixture of orthoclase, plagioclase, and quartz in large quantity, with brownish-black hornblende crystals, biotite, and very rarely iron pyrites. The hornblende crystals occasionally exhibit very sharply defined hexagonal outlines ($\infty \bar{P} \infty$).

Syenite-granite from between Sauk Rapids and St. Cloud.—Identical with the last described. On some specimens a black mineral was observed, closely resembling allanite or orthite in its physical properties.

Porphyritic-syenite-granite from Watab.—Is a rock which consists of a moderate to coarse grained "ground-mass," containing large crystals of reddish orthoclase enclosed in plagioclase. The granular "ground-mass" consists of quartz, reddish hornblende, and plagioclase, with some greenish-black hornblende, and probably a few grains of magnetite and titanite. Apatite occurs acicular, enclosed in all the constituents. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	
70·05	15·04	1·70	1·09	1·97	0·82	5·09	4·77	0·81	= 101·34

P_2O_5 = 0·07.

From the analysis it is clear that this rock is the most acid of the series, being rich in quartz.

The authors sum up the constitution of the syenitic-granites briefly as follows, viz., "They consist of quartz, orthoclase, oligoclase, with a little hornblende, biotite, apatite, and some magnetite and titanite. The hornblende crystals are sometimes characterised by the occurrence of an inner kernel of a dichroitic mineral, which is probably augite (diallagite). The rocks are porphyritic in character, and not syenite proper, as the amount of hornblende is too low."

The conclusions arrived at from the authors' investigations on the hornblendic rocks of Minnesota are as follows. In Minnesota there occur a complete series of basic and acid rocks which contain an augitic mineral (diallagite) in conjunction with the hornblende, and also quartz and orthoclase. They cannot decide whether the hornblende was derived from augite or not, but they point out the resemblance of those rocks to those described as "Syenite from Scharfenstein* (vom Rath, *Zeitsch. Geol. Reichs-Austalt,* 1875, xxv, 217), and also by the same author (*Pogg. Ann.*, 144, p. 248), as diorite passing into gabbro, through the taking up of diallagite. C. A. B.

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* (Kalkowsky, *Jahrb. f. Min.*, 1876, 140), "Augite-Syenite from Monzoni."

Organic Chemistry.

A New General Synthetical Method of Producing Hydrocarbons, &c. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, lxxxiv, 1392—1395).—When to amyl chloride small quantities of anhydrous aluminium chloride are added, there occurs a brisk disengagement of hydrochloric acid gas, accompanied by hydrocarbons which are not absorbed by bromine. The liquid divides into two layers, and, on the completion of the reaction one of these is found to contain an extremely varied series of hydrocarbons, ranging from highly volatile bodies to products having a boiling point above that of mercury. The lower members of the series belong to the hydrocarbons C_nH_{2n+2}, while the higher members are richer in carbon. When the above reaction was made to take place in presence of a hydrocarbon, it was easy to obtain a combination of the radicle of the organic chloride with the hydrocarbon, less the hydrogen replaced. Thus, the authors mixed amyl chloride with a considerable excess of benzene, and having added aluminium chloride by small quantities at a time, they obtained, by fractional distillation of the products, a liquid boiling at 185—190°, and having the composition and properties of amyl-benzene, $C_6H_5.C_5H_{11}$. By using ethyl iodide instead of amyl chloride, ethyl-benzene was obtained, together with many compounds having a high boiling point. Similarly, by operating under proper conditions with benzene and methyl bromide or chloride, toluene and other higher derivatives of benzene were obtained. The other halogen salts of aluminium gave reactions analogous to those of the chloride. R. R.

An Absorbent of Carbon Monoxide. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, x, 1122—1123).—On passing pure carbonic oxide into pure anhydrous hydrocyanic acid, carefully cooled, it was found to be rapidly absorbed. The product was not miscible with concentrated hydrochloric acid, but on removing it from the freezing mixture carbonic oxide was evolved in a regular stream. On gently warming, the gas is given off more rapidly, and ultimately the liquids mix, when the evolution of gas becomes stormy. The author was in hopes of obtaining glyoxylic acid, but none could be detected. C. E. G.

On Partial Decomposition and the Formation of Ethers. By JULIUS THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1023—1026).—In a paper on the formation of ethers (p. 418 of this volume), van't Hoff has described the partial decomposition of the alcohols by the acids; and in a paper on Berthollet's theory of affinity (*Pogg. Annalen*, cxxxviii, 65) the author has treated of the partial decomposition of salts by acids. Both have arrived at exactly the same formula for expressing the amount of decomposition, and the constants of the two formulæ agree. The formation of ethers and the partial decomposition of salts by acids in aqueous solution follow the same laws. G. T. A.

Reactions of certain Fatty Bodies under Energetic Chlorination. By F. KRAFFT (*Deut. Chem. Ges. Ber.*, x, 801—806).—It is already known that hexyl iodide can be readily converted into perchlorobenzene. This is interesting, on account of the striking proof which it furnishes that the energetic action of chlorine on hydrocarbons not only leads to a splitting up of the carbon nucleus, but that if excess of chlorine be avoided, a closer and firmer binding together of the carbon-atoms results. In the first place the prominently interesting circumstance is pointed out that on perchlorination the most stable decomposition-products appear together, such as perchloromethane, perchlorethylene, perchlorethene, perchlorobenzene, and the long known condensation-series of perchloromethane. This appears to be the actual result of experiences gained in the field of perchlorination. The conversion already mentioned, of hexyl iodide into perchlorobenzene, finds its most probable expression in the final equation:—

$$(I.)\quad C_6H_{13}I + 10Cl_2 = C_6Cl_6 + 13HCl + ClI.$$

Of course this equation, like all of the kind, merely exhibits the ingredients on one side, and the final products on the other, but does not touch upon the mechanism of the process with its series of associations and dissociations. The inverse reaction, viz., the conversion of perchlorobenzene into hexane has already been realised by Berthelot. It thus becomes probable from the outset that the above process takes place without intermediate splitting up, and that we have here to do with an alternation of additions of chlorine on the one side, and separations of hydrogen chloride on the other. The author has lately made the observation that perchlorobenzene is never the exclusive product of the reaction. With the bye-products, when only in small quantity, perchloromethane was mostly found, and a little of a body not yet investigated, having a peculiar odour. In another preparation of perchlorobenzene, a somewhat greater quantity of hexyl iodide was employed, and a shorter time allowed for the heating in the tube. A smaller yield of perchlorobenzene was the result. The oil, formed now in greatest quantity, was purified by distillation. First perchloromethane passed over in considerable quantity; perchlorethane could not be detected; the remainder almost all distilled over from 270° to 290°. This last product on standing yielded crystals; and when strongly cooled solidified for the most part to a crystalline mass, fusing again at the heat of the hand. In this case the condensation had evidently not proceeded to the formation of perchlorobenzene, but only to that of perchloromethane and another hydrocarbon chloride. About the same time it was observed that by perchlorinating such bodies as oenanthol, oenanthylic acid, and oenanthyl chloride, there was always formed, besides perchlorobenzene, more or less of the hydrocarbon chloride boiling at 280°, with varying quantities of perchloromethane.

To obtain this new hydrocarbon chloride, hexyl iodide in portions of 10 grams at a time was heated in sealed tubes with addition of nearly equal quantities of iodine, in such a manner that the action of the iodine chloride was exhausted first at 100—120°, and then the temperature was allowed to mount gradually to about 240°, till the iodine trichloride which was continually regenerated appeared to be no more acted upon.

Under these conditions no perchlorobenzene is formed, a further very remarkable complication setting in. The new chloride was now purified by fractional distillation, passing over below 290°. To separate it from still adhering perchlorethane, the original mixture of chlorides is placed in a tubulated retort, and gradually heated in the paraffin-bath to 200—223°. The perchlorethane then escapes completely but slowly; in fact, some hours must be allowed for it. At length the heating is stopped, and the retort left to cool. The substance then solidifies after some time. Just before this solidification takes place, the perchlorethane which covers the neck of the retort may be easily removed with a pipette. The above distillation or heating must be repeated to remove the last traces of perchlorethane, the purity of the product being tested by inserting a glass rod, which should no longer become covered over with little stellate crystals of a camphor-like odour, but with slowly solidifying oily drops, or drops which do not solidify. The product is a quite colourless crystalline body, forming in flat vessels twin-crystalline plates. It may be freed from impurities by pressure. This body has the composition C_4H_6, and may be called provisionally* *perchloromesol*, because of its genetic relations to perchlorethane and perchlorobenzene, holding a kind of mid-position between them. In water this body is not soluble, but it crystallises from alcohol, on standing and cooling the solution, in thin shining prisms often of considerable length. When the crystallisation is hastened by dropping in the fragment of a crystal, the whole suddenly solidifies to a pasty mass, consisting of fine needles. Melting point = 39°. Perchloromesol distils over, with very slight decomposition and evolution of chlorine, between 283—284° (bar. ·733 mm.). Under the same conditions perchlorobenzene distils at 310° (uncorrected). Perchloromesol is far less volatile than perchlorethane, and does not sensibly diminish on exposure in the air. Its odour is much fainter than that of perchlorethane, and resembles that of turpentine more than that of camphor. At a very high temperature, like all lower hydrocarbon chlorides, it forms perchlorobenzene. It appears to be as little affected by iodine trichloride as perchlorethane or perchlorobenzene.

Investigations carried out with a series of fatty bodies, have shown that the formation of perchloromesol by perchlorination under special conditions, is almost as general as that of perchlorethane or perchlorobenzene. These conditions refer to the necessity of raising the temperature finally for further action of the chlorine, especially with molecules richer in carbon.

These results give increased importance to the fact that crotonylene, the hydrocarbon which corresponds in all probability with perchloromesol, occurs in coal gas, together with pyrogenic hydrocarbons like methane, ethene, acetylene and benzene, and is formed by the condensation of ethene and of acetylene. From all this it appears that perchloromesol plays the same part in the condensation series of the hydrocarbon chlorides, as for example perchloromethane. The decomposition of the hexyl iodide to form perchloromesol, takes place (at least in its last phases) by processes quite independent of those giving rise to perchlorobenzene;

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* *Note by Abstractor.*—As the author further on remarks that crotonylene, C_4H_6, is the hydrocarbon which is in all probability analogous to perchloromesol, it seems a pity that this idea did not suggest to him a more appropriate and scientifically consistent name than perchloro*mesol*. Why did he not call it perchlorocrotonylene? The name "perchloromesol" suggests the idea that the body in question is in some way related to the mesitylene-group, with which, however, it has nothing in common.—W. S.

$$\text{(II.)} \quad C_6H_{13}I + 14Cl_2 = C_4Cl_6 + 2CCl_4 + 13HCl + ClI.$$

It has been already mentioned that perchlorethane often appears, besides perchloromesol, as a decomposition product. Perchlorethane, however, is often quite missing when perchloromesol is present. This fact indicates that the formation of perchlorethane from hexyl iodide is quite independent of that of perchlormesol, and a further equation is necessary, in which *à priori* only the proportional quantities of perchlorethane and perchloromethane remain doubtful:

$$\text{(III.)} \quad C_6H_{13}I + 17Cl_2 = 2C_2Cl_6 + 2CCl_4 + 13HCl + ClI.$$

That the process can go on in this manner is shown by the fact that normal butyl iodide heated with excess of iodine chloride to 250°, is easily converted into perchlorethane—

$$C_4H_9I + 11Cl_2 = 2C_2Cl_6 + 9HCl + ClI.$$

W. S.

Reduction of Organic Haloïd Compounds by Zinc and Zinc-dust. By A. SABANEJEFF (*Bull. Soc. Chim.*, xxvii, 446).—At ordinary temperatures the product of the reaction of granulated zinc on an alcoholic solution of tetrabromated acetylene is dibromacetylene, whilst at higher temperatures the reduction is complete and acetylene is formed. Zinc acts in an analogous manner on ethylene bromide and propylene bromide, but it is without action on trimethylene bromide. In presence of water, zinc decomposes chloroform with liberation of marsh-gas, thus:—

$$2CHCl_3 + 3H_2O + 3Zn_2 = 2CH_4 + 3ZnCl_2$$

and ethyl iodide is easily reduced to ethane. R. R.

Normal Propylene. By E. REBOUL and E. BOURGOIN (*Compt. rend.*, lxxxiv, 1395—1398).—As succinic acid in alkaline solution splits up, under the influence of an electric current, into ethylene and carbonic acid, the authors hoped, by the electrolysis of potassium pyrotartrate, the superior homologue of the succinate, to obtain carbonic acid and trimethylene. The products collected at the positive pole were, however, found to be only a mixture of oxygen, carbonic acid, and carbonic oxide gases. Trimethylene bromide also failed to yield trimethylene, by treatment either with sodium or with nascent hydrogen. R. R.

The Inability of Propylene to Combine with Water. By E. LINNEMANN (*Deut. Chem. Ges. Ber.*, x, 1111—1121).—Siersch, on decomposing normal propylamine nitrite by boiling it with water, found that, besides nitrogen and nitrosodipropylamine, a mixture of alcohols was formed: this, when submitted to distillation, yielded a fraction boiling at 89—96°, and another boiling at 81—85°, which he considered to be pseudopropyl alcohol. Meyer and Foster have recently repeated this experiment and obtained, besides nitrogen and nitrosodipropylamine, propyl alcohol, pseudopropyl alcohol, and propylene; moreover, butylamine nitrite is decomposed in a manner precisely similar. Meyer lays great stress on the formation of propylene and butylene in these reactions, and considers that the formation of the secondary alcohol is due to the union of the olefine with water. It seemed to the author, therefore, a point of the greatest importance to obtain some evidence of the behaviour of propylene with water under various circumstances, especially as if the two did unite, they might form either pseudopropyl or normalpropyl alcohol.

In the first series of experiments the action of water at 100° on nascent propylene was tried by heating pure propylene bromide with zinc and water; propylene and hydrogen were evolved in abundance, but no propane. The hydrogen is formed by the action of zinc bromide on the metallic zinc in presence of water, zinc oxide being separated; in this way a comparatively small quantity of zinc bromide will yield a large quantity of hydrogen. If the zinc is not free from arsenic, the propylene evolved in this reaction will be contaminated with arseniuretted hydrogen, and lead to an error in the determination of the amount of propylene evolved from a given weight of propylene bromide. Two experiments were made with every precaution, in both of which the quantity of propylene evolved was found to be only 5 per cent. less than that required by theory. A large quantity of propylene bromide (430 grams) was then decomposed in a similar manner, and the evolved gases were carefully washed, but neither in the retort nor in the wash-water could any trace of an alcohol be detected.

In the second series of experiments, propylene bromide was heated at 100° with zinc and a solution of potassic hydrate, the reaction being:—

$$C_3H_6Br_2 + Zn + 4KHO = C_3H_6 + 2H_2O + 2KBr + Zn(KO)_2.$$

In this case the nascent propylene is brought in contact with nascent water, at 100°. The analytical results showed that the propylene evolved fell short of the theoretical amount indicated in the above equation by about 12 to 16 per cent., but not a trace of any alcohol could be discovered. These experiments prove conclusively that at 100°, nascent propylene does not combine with water, even if the latter be nascent. The author has not yet succeeded in ascertaining what is the cause of the amount of propylene given off being less than that indicated by theory.

The latter part of the paper is occupied by a discussion of alleged misstatements on the part of Meyer and Foster, and of Meyer, Barbieri, and Forster, with regard to the results obtained by the author in the decomposition of normal propylamine nitrite and normal butylamine nitrite. C. E. G.

Preparation of Allyl Iodide and of Acetic Anhydride. By SAYTZEFF and KANONNIKOFF (*Bull. Soc. Chim.*, xxvii, 433).—Allyl iodide was prepared from 1,000 grams of iodine, 3,000 of glycerin, and 300 of phosphorus. The phosphorus was added to the mixture of glycerin and iodine, in small quantities at a time. The distillation was carried on in a current of dry carbonic acid gas, in order to prevent any explosion. The quantity of C_3H_5I obtained about 1150 grams, whilst Claus and Oppenheim's method would yield only 700 grams.

Acetic anhydride was prepared by the action of acetyl chloride on crystallisable acetic acid. Half the theoretical quantity, in a perfectly pure state, was thus obtained. R. R.

Retarding Action of Glycerin.—By DUNN (*Chem. News*, xxxvi, 88).—The action of a glycerin solution of iodine on iron was tried. Four cylinders were taken, and into each was put 25 c.c. of a solution of iodine in iodide of potassium. They were then made up to 50 c.c., two with water and two with glycerin. A piece of iron wire was then placed in each; in two, the iron wire was suspended near the surface of the fluid, and in the others, it was placed at the bottom.

The water solutions were found, after a week, to have been acted on much more rapidly than the glycerin solutions, the difference being most marked in the case of those in which the wire was at the surface. In all the cylinders, however, the wire became covered with bubbles of gas, so that the protective action of the film of gas is not eliminated by using iodine. By using bromine instead of iodine, the iron was rapidly attacked in the water cylinders, but the action in the glycerin solution appeared to be complicated by other reactions; the bromine in one cylinder was completely decolorised save at the bottom, and in the other, the colour was paler than originally. In this case, also, bubbles of gas were observed, larger and fewer in the water solutions than in the glycerin solutions. D. B.

Crystallised Grape-sugar. By HALSE and STEINER (*Chem. News*, xxxvi, 87—88).—In 1875, a cargo of starch-sugar was returned from Australia and offered for sale in England, when it was found to be partially crystallised and to resemble cane-sugar, and it actually was taken as such. The authors for this reason obtained samples, which were analysed. The samples were of three different sorts—amorphous, amorphous with superficial crystallisation, and others completely crystallised. The amorphous substance, similar to starch-sugar, is greyish-white with stripes of brown passing through it. It feels dry, is hard, and slightly hygroscopical. The second sample consisted of amorphous dark-brown lumps of a very pasty nature, with completely developed crystalline groups (rosettes) imbedded in them, and a yellow, very well crystallised thin crust on some parts of the surface. The rosettes are of the size of a bean up to that of a chestnut, and have a clear amber or pale-yellow colour, with a fatty glance. To free the rosettes from the adhering amorphous substance, they were first immersed in dilute alcohol, then dipped in absolute alcohol, and subsequently dried with filter paper. The third kind of sample was in completely crystallised compact pieces, remaining dry in the air, and being very hard. By treatment with alcohol, a part of the mass was dissolved out and a network of the larger warty crystals of an amber-yellow colour was obtained, while the pieces of the very fine crystallisation are of very much darker colour, and soluble in alcohol. The following are the results of the analyses:—

Crystals.

	Rosettes.	Nodules of the size of a bean.	Nodules smaller.	$C_6H_{12}O_6 + H_2O$ corresponding to.
Ash......	trace	trace	trace	—
Water....	9·45	9·26	9·45	9·09
Glucose ..	90·35	90·45	90·20	90·91
Dextrin ..	0·20	0·29	0·35	—
	100·00	100·00	100·00	100·00

Samples.

	Amorph. with rosettes.	Amorph. without rosettes.	Fine crystallised.	Warty, small.	Warty, larger.	Amorphous.
Ash	0·36	0·37	0·33	0·29	0·15	0·45
Water	12·00	12·20	11·80	11·20	10·50	8·60
Glucose ...	80·10	78·60	81·40	84·60	85·00	83·90
Dextrin ...	1·74	1·90	1·53	0·79	0·68	1·54
Optic inact. subst. ..	5·80	6·93	4·94	3·12	3·67	5·51
	100·00	100·00	100·00	100·00	100·00	100·00

In considering the results of the analyses of the samples with the warty crystals, the author mentions that only an increase of sugar takes place with the growth of the crytallisation, and it may also be assumed that if the adherent amorphous mass could be completely separated from the crystals, the latter would represent pure grape-sugar. The darkening of the amorphous mass may have been effected by the combined action on partly caramelised products, of moisture, lime, and of the ammonia liberated by the putrefaction of the albuminous matter (gluten) present. A long voyage in a tropical climate furnished not only the necessary conditions for the melting of the substance and for the development of ammonia, but was also favourable to such a slow crystallisation as grape-sugar requires. Once the crystallisation introduced, a continual growth took place.

D. B.

Optically Inactive Sugar. By W. E. HALSE and E. STEINES (*Chem. News*, xxxvi, 107).—A sample of molasses, the drainings of molasses into a ship's hold, and consequently mixed with bilge-water, had the following composition: organic matter, 42·50 p. c.; water, 51·75 p. c.; ash, 5·75 p. c. After clarification with subacetate of lead, it reduced copper solution to an amount equal to 27·70 p. c. of glucose. It was optically inactive. To decide whether it was a mixture of levulose with dextrose or saccharose, it was partially fermented, and even then remained without action on polarised light. Even after treatment with caustic soda to destroy levulose, it remained inactive. The only possible conclusion accordingly is that the sugar was an inactive modification. W. R.

Action of Acid Chlorides on Organo-Zinc Compounds. By D. PAWLOW (*Liebig's Annalen*, clxxxvii, 104—143).—*Formation of Ketones.*—The author has made quantitative experiments on the production of acetone by the reaction of acetic chloride with zinc methide. He finds that with 2 mols. of the chloride to 1 mol. of zinc methide, the yield of acetone is about 80 per cent. of the theoretical amount, and that the yield is not greatly increased by employing larger proportions of zinc methide. The reaction of 2 mol. R'COCl with 1 mol. Zn R'_2 may serve for the synthesis of ketones in general, but for the preparation of the pinacolins (of which tertiary butyl-methyl ketone is the simplest) it is advantageous to employ $1\frac{1}{2}$ or 2 mol. of the zinc-compound to 1 mol. of acid chloride, on account of the greater cost of the latter.

Synthesis of Tertiary Alcohols containing three Different Radicles.—The first known representatives of this class of bodies, *methyl-ethyl-propyl carbinol* and *methyl-ethyl-isopropyl carbinol*, have been obtained by the author by the reaction of butyric chloride or isobutyric chloride on a mixture of zinc methide and zinc ethide, and subsequent decomposition of the product with water.

Methyl-ethyl-propyl carbinol is a colourless liquid, having a faint camphor-like odour, and boiling at 135-138°. It forms with gaseous hydrogen iodide a compound which, by treatment with alcoholic potash, yields the corresponding heptylene. The latter is a colourless liquid, smelling like amylene and boiling between 90° and 95°; it combines with bromine to form the compound $C_7H_{14}Br_2$.

Methyl-ethyl-isopropyl carbinol boils at 124—127°. It forms with hydrogen iodide a compound which is decomposed by alcoholic potash, yielding a heptylene boiling at 75—80°, and combining with two atoms of bromine.

By-products in the Preparation of Ketones.—In the reactions of acid chlorides with organo-zinc compounds, there are formed, besides ketones and tertiary alcohols, certain products of high boiling-point, the nature of which has not hitherto been made out. These substances the author finds to be condensation-products of ketones, formed by the direct action of the zinc-compounds. Thus, for instance, zinc ethide or methide acting on acetone produces mesityl oxide:

$$2C_3H_6O + ZnR_2' = C_6H_{10}O + 2R'H + ZnO.$$

Mesityl oxide, however, is not the only product thus formed from acetone. It seems probable that further condensation takes place, owing to the elimination of more water, higher products being thus formed.

Some Bodies analogous to Mesityl Oxide.—1. A substance having the formula $C_8H_{14}O$ is formed, together with methyl-ethyl-ketone, by the reaction of equal numbers of molecules of propionic chloride and zinc methide. It is a colourless liquid, insoluble in water, boiling at 167—168°. Sp. gr. 0·877 at 0°; 0·862 at 18°. Its formation from methyl-ethyl-ketone may be represented by the equation:—

$$2C_4H_8O - H_2O = C_8H_{14}O.$$

This substance forms with hydrogen iodide a heavy dark-coloured oil, represented by the formula $C_8H_{15}IO$.

2. Similarly, the compound $C_{10}H_{18}O$ is formed as by-product in the reaction between isobutyric chloride and zinc methide. It is a colourless liquid of peculiar odour, insoluble in water, boiling at 189—191°. Sp. gr. 0·87 at 0°; 0·855 at 20°. It combines with hydrogen chloride to form a yellowish oily body ($C_{10}H_{19}ClO$) having the odour of turpentine; and with hydrogen iodide to form a dark coloured crystalline body.

3. A by-product having the formula $C_{12}H_{22}O$ is formed in the preparation of dimethyl-isobutyl carbinol. It is a colourless liquid, insoluble in water, boiling at 217—219°. Sp. gr. 0·864 at 0°; 0·849 at 20°. Like the two preceding bodies, it combines with hydrogen chloride and iodide.

All these compounds combine with bromine, and may, therefore, be regarded as non-saturated ketones. Their chemical structure has yet to be made out. J. R.

Constitution of Cyanamide. By M. FILETI and R. SCHIFF (*Gazetta chimica italiana*, vii, 204—209).—It has long been a question as to whether the formula, $CN.NH_2$ or $HN{=}C{=}NH$, represents the constitution of cyanamide. The first, however adapts itself most readily to the explanation of the formation of cyanamide by the action of ammonia on cyanogen chloride: $CN.Cl + NH_3 = CN.NH_2 + HCl$, and also by the desulphuration of sulphurea, $S{=}C(NH_2)_2 = CN.NH_2 + H_2S$, whilst Mulder urges that the existence of the silver derivative of cyanamide, CN_2Ag_2, requires cyanamide to have the formula, $HN{=}C{=}NH$, as only in imides can the hydrogen be displaced by metals. This argument, however, is not conclusive, as several amines and amides containing metals exist, such as the sodio-amides and anilines, and argento-acetamide. Moreover, aldehyde, as Knop has shown, acts on cyanamide, giving a derivative of melamine, which cannot be explained with the imide formula. Again, amides unite with chloral, forming substitution-products of chloral-ammonia, whilst no compound of chloral with an imide is known. This reaction takes place with cyanamide, affording strong evidence that it is an amide of the formula $CN.NH_2$. Cyanamide dissolves in chloral with development of heat, and the syrupy product, after being allowed to stand for 24 hours, and then heated at 100°, solidifies, and at the same time swells up to about 20 times its bulk. It is soluble in alcohol, ether, and chloroform, but separates as a resin. The authors consider the syrupy product as a simple product of addition, CN.NH.CH(OH).CCl_3, whilst the solid has probably triple that formula, and is a product of the addition of melamine.

When the diargentic compound of cyanimide is heated with ethyl iodide, silver iodide is formed, and a red liquid which, from the results of analysis and its boiling point, was proved to be diethylcyanamide. Heated for some time with hydrochloric acid, the crude product yielded a mixture of ammonium chloride and diethylamine hydrochloride.

These results prove that the only possible formula for cyanamide is CN.NH_2. C. E. G.

Absence of Rotatory Power in Iodide of Triethyl-methyl-stibine.

By J. A. LE BEL (*Bull. Soc. Chem.*, xxvii, 444, 445).—The dextrogyratory power attributed to iodide of triethyl-methyl-stibine, was indeed found to exist in a sample prepared by the author, but to be extremely small. As, however, its presence contradicts the law which asserts that optically active compounds cannot be formed without some optically active constituent, the author sought for such a constituent among the substances used in the preparations. He found it in the commercial alcohol, which is contaminated with more or less amylic alcohol, an optically active substance. On submitting the alcohol used in the preparation of the ethyl iodide to a process by which the optical power of the contained amylic alcohol was obviated, the author was able to prepare iodide of triethyl-methyl-stibine in which no rotatory power could be detected. R. R.

Formation of Sulphinic Acids of the Fatty Group from the Chloranhydrides of the Sulphonic Acids.

By C. PAULY (*Deut. Chem. Ges. Ber.*, x, 941—943).—Schiller and Otto having shown that the chloranhydrides of the aromatic sulphonic acids (benzene-sulphonic and paratoluene-sulphonic acids) could easily be converted into the zinc salts of the sulphinic acids by the action of zinc dust, it was thought interesting to determine whether this method could be applied to the preparation of sulphinic acids of the fatty group. Accordingly the author has studied the behaviour of the ethyl- and isobutyl-sulphochlorides towards zinc-dust, and found his expectations realised, the sulphinic zinc salts being formed just as readily as those in the aromatic series.

I. *Ethyl-sulphinic Acid*, $C_2H_6SO_2$.—Ethyl sulphochloride and zinc dust were allowed to react under water, which took up the sulphinic zinc salt formed. This salt was purified by evaporation of the solution, out of which it crystallised, and then it was recrystallised from alcohol. It possessed the composition and properties of the zinc ethyl-sulphinate, described by Wischin as prepared by the action of sulphur dioxide on zinc-ethyl. Analysis yielded numbers agreeing with the formula, $(C_2H_5SO_2)_2Zn + H_2O$.

The barium and sodium salts were prepared from this zinc salt, analysed and identified. Both salts crystallised with difficulty. The sodium salt was deliquescent.

II. *Isobutylsulphinic Acid,* $C_4H_{10}SO_2$.—The isobutyl sulphochloride was prepared by the action of phosphorus pentachloride on potassium isobutylsulphonate, the sulphonic acid by oxidation of the mercaptan with nitric acid. The sulphochloride is a colourless, tolerably mobile liquid, heavier than water, and not decomposed by the latter in the cold. By taking small quantities at a time, it may be distilled without decomposition (between 189° and 191°, uncorrected). Its vapours have a penetrating odour, and strongly irritate the mucous membrane. Analysis confirmed the formula, $C_4H_9SO_2.Cl$.

It was converted into zinc sulphinate by treatment with zinc-dust under water, like the ethyl sulpho-chloride. This salt was extracted from the frothy mass by boiling water, and recrystallised from alcohol.

Zinc isobutylsulphinate forms white and tolerably large plates, with a mother-of-pearl lustre, freely soluble in hot water and alcohol, sparingly in cold. The salt obtained from alcohol is anhydrous, but from water it appears to separate with water of crystallisation. Analysis confirmed the formula, $(C_4H_9SO_2)_2Zn$, (crystallised from alcohol).

The *sodium salt* crystallises with difficulty, and is easily soluble in water and alcohol. It forms thin hygroscopic plates. The *isobutylsulphinic acid* prepared from this salt by addition of sulphuric acid, shaking with ether, &c., forms a faint yellow syrup, strongly acid, bleaching litmus paper, and easily soluble in water. After long standing in the exsiccator it showed no disposition to crystallise. The *barium salt*, prepared from the free acid, is very soluble in water, like the sodium salt, also in alcohol, and crystallises with difficultly. Nascent hydrogen easily converts the isobutylsulphinic acid into the corresponding mercaptan. W. S.

Behaviour of Sodium Acrylate with Fused Potash. By E. LINNEMANN (*Deut. Chem. Ges. Ber.*, x, 1121—1122).—In 1873 the author stated that Redtenbacher's observation that sodium acrylate gave acetic and formic acids when fused with potassium hydrate, was incorrect, since he found that this salt was carbonised when added to the fused alkali. As, however, acrylic acid when heated with a solution of sodium hydrate yields ethylenelactic acid and hydracrylic acid, and the latter is decomposed by fusion with potash, giving rise to acetic and formic acids, it is evident that if Redtenbacher had evaporated a solution of potassium hydrate to which he had added the sodium acrylate, and subsequently fused the mixture; or if the potash had contained so much water that it fused below the temperature at which sodium acrylate is decomposed, a hydracrylate would have been formed and subsequently converted into acetate and formate. From Redtenbacher's description, however, it does not appear in what way he conducted the experiment. C. E. G.

On the Non-saturated Acids. By RUDOLPH FITTIG. Part I. (*Liebig's Annalen*, clxxxvii, 42—104).—1. *The Crotonic Acid from Citraconic and Mesaconic Acids.*—Citraconic anhydride, when heated to

100° with hydrochloric acid saturated at 0°, is partially converted into citrachloropyrotartaric acid, which is resolved by boiling with strong soda-ley into an acid having the composition of crotonic acid, $C_4H_6O_2$, but differing in properties from any of the three known varieties of that body. The product crystallises from water, in which it is easily soluble, in long, colourless prisms, which melt at 16°. It has a strong but not unpleasant odour, dissolves in all proportions of alcohol and ether, and boils constantly at 160·5°.

The *calcium salt* $(C_4H_5O_2)_2Ca$, crystallises in tufts of long colourless needles, easily soluble in water.

The *silver salt*, $C_4H_5O_2Ag$, precipitated by silver nitrate from the calcium salt, crystallises from boiling water in long needles or in small compact crystals, which are scarcely affected by light. It dissolves sparingly in cold, and more freely in hot water. The dry salt does not lose weight at 70°, but about 100° a sudden decomposition takes place throughout the mass, the odour of the acid being evolved.

The acid is completely decomposed by melting potash at a comparatively low temperature, being resolved into propionic acid and carbon dioxide only.

Mesaconic acid heated to 140° with strong hydrochloric acid, is converted into mesachloropyrotartaric acid; and the latter, by boiling with soda-ley, yields a crotonic acid identical with that obtained from citraconic acid.

2. *Methacrylic Acid.*—The author has compared the crotonic acid obtained as above with methacrylic acid, and finds that the two are identical in their properties and in the characters of their salts.

Methacrylic acid is completely converted into isobutyric acid by the action of sodium-amalgam at the ordinary temperature. This fact agrees with the observation of Gromont and Swarts, that Kekulé's monobromocrotonic acid obtained from citradibromopyrotartaric acid is converted by the action of sodium amalgam into isobutyric acid.

Methacrylic acid dissolves in concentrated hydriodic acid at the ordinary temperature, forming a clear solution. When the hydriodic acid is in large excess, the solution deposits, after some time, tufts of long prisms consisting of *iodisobutyric acid*, $C_4H_7IO_2$ This body dissolves easily in carbon bisulphide, and crystallises therefrom in brilliant tablets. It melts at 36°.

3. *Xeronic Acid, a new derivative of Citraconic Acid.*—Xeronic acid is the name given by the author to an acid, the anhydride of which is formed, together with citraconic anhydride, in the distillation of citric acid. Xeronic anhydride is formed whenever citraconic anhydride is distilled. Citraconic anhydride begins to boil at 212°, and the greater part of it distils about that temperature; but at the same time a constant evolution of carbon dioxide takes place, and the temperature gradually rises until, at 250°, there passes over a yellow oil consisting chiefly of a mixture of citraconic and xeronic anhydrides. The decomposition of citraconic anhydride goes on even below its boiling point, direct experiment having shown that carbon dioxide is slowly and regularly evolved at 160°.

Xeronic Anhydride, $C_8H_{10}O_3$, is a colourless liquid of peculiar odour, boiling at 242° (mercury entirely in vapour), and remaining liquid at

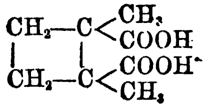
— 18°. It distils readily with water, in which it sinks, dissolving sparingly. In alcohol and ether it dissolves easily. The corresponding acid appears not to exist in the free state, but to break up, like carbonic, sulphurous, and arsenious acids, into the anhydride and water. Hence the name (from ξηρός, dry). The anhydride does not combine with water. A dilute solution of the sodium salt, when acidified with hydrochloric acid, is clear at first, but after a time becomes turbid and deposits the anhydride.

The *silver salt* $C_8H_{10}O_4Ag_2$, thrown down by silver nitrate from a solution of the anhydride in ammonia, is a heavy, white, pulverulent precipitate, very sparingly soluble in boiling water, and not affected by light.

The *calcium salt*, $C_8H_{10}O_4Ca + H_2O$, is the most characteristic of the salts of xeronic acid, and serves admirably for the detection of the acid, and for the separation of this from other acids. It is easily obtained by dissolving xeronic anhydride in ammonia, driving off excess of ammonia by boiling, and adding calcium chloride. At ordinary temperatures the solution remains clear, even after long standing; but when gently heated, it becomes turbid, and on boiling for a short time, the whole of the calcium salt is deposited in the form of a flocculent precipitate, which afterwards turns crystalline. The salt thus obtained is soluble only in a very large quantity of water. It gives off half a molecule of water at 130—140°, and the rest at 170°.

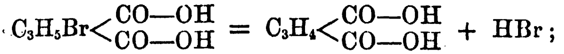
The *barium salt*, $C_8H_{10}O_4Ba + \frac{1}{2}H_2O$, is obtained in the same manner as the calcium salt, which it resembles in every respect. It loses its water at 140°.

Xeronic acid is shown by the composition of its salts to be a dibasic acid of the formula $C_6H_{12}O_4 = C_6H_{10}{<}\begin{smallmatrix}COOH\\COOH\end{smallmatrix}$, breaking up, however, when set free, into water and the anhydride, $C_6H_{10}{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}O$. It is homologous with citraconic acid, but behaves in an entirely different manner. It combines neither with nascent hydrogen nor with bromine, and therefore does not belong to the so-called non-saturated acids. Seeing that xeronic acid is polymeric with methacrylic acid, and that citraconic acid is resolved, in certain circumstances, into carbon dioxide and methacrylic acid, whilst xeronic anhydride is likewise produced from citraconic anhydride by elimination of carbon dioxide, it seems very probable that xeronic acid is formed by the union of two molecules of methacrylic acid, and is constituted in accordance with the formula—



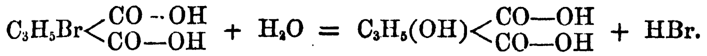
4. *Addition-products of Itaconic, Citraconic, and Mesaconic Acids.*— Itaconic acid, in fine powder, is converted by contact for a few days with fuming hydrobromic acid (in which it does not dissolve) into small hard crystals of itabromopyrotartaric acid, melting at 137°.

This product, when heated with water, is completely resolved into itaconic and itamalic acids and hydrogen bromide:



$$C_3H_5Br<\begin{array}{l}CO—OH\\CO—OH\end{array} = C_3H_4<\begin{array}{l}CO—OH\\CO—OH\end{array} + HBr;$$

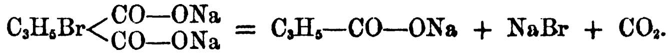
Itaconic acid.



$$C_3H_5Br<\begin{array}{l}CO—OH\\CO—OH\end{array} + H_2O = C_3H_5(OH)<\begin{array}{l}CO—OH\\CO—OH\end{array} + HBr.$$

Itamalic acid.

Citraconic acid and its anhydride dissolve readily in fuming hydrobromic acid, and in the course of a few days are converted into hard, shining crystals of citrabromopyrotartaric acid melting at 148°. On prolonged boiling of its aqueous solution, this substance gives off the whole of its bromine as hydrogen bromide, and is resolved into methacrylic and mesaconic acids: in alkaline solution, it is decomposed much more rapidly on warming, yielding almost exclusively methacrylic acid:



$$C_3H_5Br<\begin{array}{l}CO—ONa\\CO—ONa\end{array} = C_3H_5—CO—ONa + NaBr + CO_2.$$

This decomposition of citrabromopyrotartaric acid affords the best means of preparing methacrylic acid, which may thus be easily obtained in large quantity.

Mesaconic acid is converted by heating to 140° with concentrated hydrobromic acid into citrabromopyrotartaric acid, identical with that formed by the action of hydrobromic acid on citraconic acid in the cold.

Dibromopyrotartaric Acids from Citraconic and Mesaconic Acids.—Bromine combines very readily with citraconic acid in the cold; with mesaconic acid only on warming. Both the products ($C_5H_6O_4Br_2$) crystallise easily: that obtained from citraconic acid melts at 150°; that from mesaconic acid, at 170°. By prolonged boiling with water, they are resolved into carbon dioxide, hydrogen bromide, and bromomethacrylic acid.

5. *Behaviour of Fumaric and Maleic Acids with fuming Hydrobromic Acid.*—Fumaric acid, when heated with concentrated hydrobromic acid in sealed tubes is converted into monobromosuccinic acid, apparently identical with that formed by the action of bromine on succinic acid. When boiled with water the brominated acid is almost entirely re-converted into fumaric acid.

Maleic acid, in fine powder, dissolves quickly in cold fuming hydrobromic acid, and is almost immediately converted into fumaric and monobromosuccinic acids in equal numbers of molecules.

Maleic anhydride behaves in the same manner.

6. *Constitution of the Non-saturated Dibasic Acids.*—The author's conclusions as to the constitution of these acids, based upon the foregoing facts, coincide with those given in a previous paper, of which an abstract appears in this volume (p. 429). J. R.

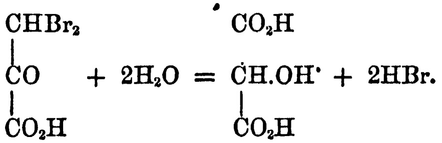
Diallyl-oxalic Acid. By M. Saytzeff (*Bull. Soc. Chim.*, xxvii, 446).—By acting on oxalic ether with zinc and allyl iodide, the author obtained diallyloxalic ether, which he heated with barium hydrate, and having removed the excess of the latter by means of carbonic acid, decomposed by sulphuric acid the barium salt which had been formed, and extracted the diallyloxalic acid with ether. The acid presents itself in minute crystals, soluble in ether and alcohol, but not readily soluble in water. These crystals melt at 48·5°, but the acid cannot be distilled without decomposition. By oxidation this acid gives rise to a resinous substance which has not yet been examined. R. R.

Glutamic Acid from the Juice of Vetch-germs. By GORUP-BESANEZ (*Deut. Chem. Ges. Ber*, x, 780—782).—It has been shown by the author and also by Cossa, that during the germination of the vetch, leucine is always formed, together with asparagin. It is, therefore, reasonable to suspect, also, the presence of tyrosine and glutamic acid in the juice of the vetch-germs. This latter acid has been already found by Scheibler in beet-root molasses. Evidently during the germination of the vetch a splitting-up of the albuminous body of the reserve-substance of the seed takes place, chemically coinciding with that which occurs during the renewal of substance in the animal economy, and likewise externally to the living organism by the action of known chemical agents. Attempts to obtain glutamic acid from the above-mentioned source were, however, unsuccessful, until a research by E. Schulze and Barbieri on the occurrence of an amide of glutamic acid in gourd-germs, suggested the proper course to be taken. The mother-liquors of the separated leucine were boiled for some hours with hydrochloric acid in a vessel with inverted condenser, and then precipitated with lead acetate in excess. The filtrate, evaporated to a small bulk, was treated with a large excess of alcohol. The precipitate of lead salts, completely separated out after twenty-four hours' standing, was thrown on a filter, washed, and then suspended in water, and a stream of sulphuretted hydrogen passed through. The hydrochloric acid in the filtrate was removed by oxide of silver, and the filtrate evaporated to a small bulk. White crystalline crusts separated gradually, having a strongly acid reaction, and reducing Fehling's solution on warming. The aqueous solution of the acid was neutralised by boiling with copper carbonate, and filtering hot. From the deep-blue filtrate the characteristic, shining, bright-blue needles of glutamate of copper separated out. These crystals contain water of crystallisation, which they lose at 140°. The formula found to coincide best with the results of analysis was $C_5H_7CuNO_4 + 2\frac{1}{2}H_2O$. The author hopes soon to obtain further results with a fresh quantity of material just prepared. There appears to be no longer any doubt as to the existence of a very soluble glutamine. Hitherto tyrosine has not been obtained in more than traces from the source afore-named. It was easily detected by L. Meyer's delicate reaction with mercuric nitrate and nitrous acid. W. S.

Action of Potassium Cyanide on Chloromaleic Ether. By A. CLAUS (*Deut. Chem. Ges. Ber.*, x, 928—930).—Continuing his researches on the action of potassium cyanide on halogenised organic compounds, the author, in conjunction with Franck, has studied the behaviour of chloromaleic ether. To prepare this ether it is recommended to take choromaleic chloride, directly prepared by heating together tartaric acid and phosphorus pentachloride, and to decompose it with absolute alcohol. After repeated distillation, the ether is then obtained as an almost colourless liquid, distilling without decomposition. Boiling point at 735 mm. bar. = 243—245° (uncorrected). Spec. grav. at 20° = 1·178. 1 mol. of the ether is treated with 3 mols. potassium cyanide dissolved in double its weight of water, and to this mixture so much alcohol is added that a clear solution is obtained. After some five minutes the liquid becomes hot and potassium chloride crystallises out, whilst the solution assumes an intensely brown colour. After several hours' standing the reaction appears to be at an end, no more chloromaleic ether separating out on addition of water. Efforts were made to isolate the cyanised products which were at first formed, but without success. Mixtures were always obtained, the separation of which could not be effected, the products when operated upon suffering a further partial conversion. Continued boiling with potash or hydrochloric acid effects the complete conversion of the originally formed or partially decomposed cyanogen-compounds, succinic acid being formed. Considering the final result in itself, the reaction with potassium cyanide is a reduction, the conversion of chloromaleic acid into succinic acid being effected by substitution of hydrogen for chlorine, and at the same time addition of hydrogen taking place. This reaction is quite analogous to that which Böttinger obtained by treating pyroracemic acid with hydrocyanic and hydrochloric acids, whereby lactic acid was produced. The simplest explanation of the foregoing accords well with an earlier assumption of the author, that at first a dicyanosuccinic acid arises, in consequence of simultaneous substitution of chlorine by cyanogen and addition of hydrocyanic acid. This dicyanosuccinic acid, on the decomposition of its cyanogen-residue, retains in the molecule, not two carboxyl groups, but simply two hydrogen-atoms, carbonic acid being given off. The study of the behaviour of monobromosuccinic and dibromosuccinic acid to potassium cyanide, which is in progress, may be expected to yield similar results.

W. S.

Tartronic Acid. By E. GRIMAUX (*Bull. Soc. Chim.*, xxvii, 440—442).—When baryta water is added to a solution of dibromated pyruvic acid, a barium salt is precipitated, which by decomposition with sulphuric acid yields a crystalline substance identical with tartronic acid, $C_3H_4O_5$. Their action may be represented by this equation:—



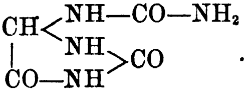
$$\begin{array}{l}CHBr_2\\ |\\ CO\\ |\\ CO_2H\end{array} + 2H_2O = \begin{array}{l}CO_2H\\ |\\ CH.OH\\ |\\ CO_2H\end{array} + 2HBr.$$

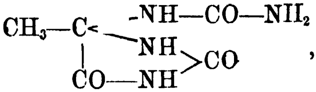
R. R.

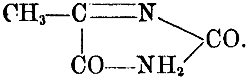
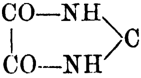
Synthetic Researches on the Uric Acid Group. By E. GRIMAUX (*Ann. Chim. Phys.*, 356—432).—The contents of this paper have been published in the *Comptes rendus*, and abstracts of the work have appeared in vols. xxvii—xxix of this *Journal.*

The following are the most important results of this investigation :—

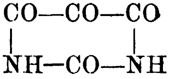
The action of aldehydic and acetonic acids on urea gives rise to compounds analogous in their properties and constitution to the true uric derivatives.

Glyoxylic diureide is identical with allantoïn,  $\begin{array}{l} CH<^{NH-CO-NH_2}_{NH}\!\!>CO \\ | \\ CO-NH \end{array}$.

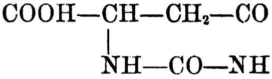
Pyvuvil,  $\begin{array}{l} CH_3-C<^{NH-CO-NII_2}_{NH}\!\!>CO \\ \quad | \\ \quad CO-NH \end{array}$, is a homologue of this body.

Monopyruvic ureide is represented thus:  $\begin{array}{l} CH_3-C{=}N \\ | \qquad\qquad >CO \\ CO-NH_2 \end{array}$. The pyruvic ureides are intimately connected with the uric series by their decomposition into parabanic acid,  $\begin{array}{l} CO-NH \\ | \qquad\quad >CO \\ CO-NH \end{array}$. The constitution of the malic ureides is similar to that of the uric derivatives.

The malic ureides are connected with the alloxanic compounds by their decomposition into iso-alloxanates—

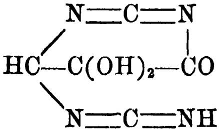


Alloxan.

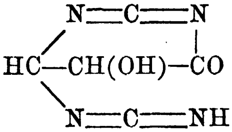


Malyluric acid.

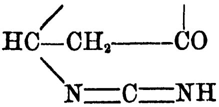
The decomposition of uric acid (1) into urea and alloxan, and (2) into allantoïn and carbon dioxide, and the reduction of the acid by nascent hydrogen to xanthine and sarcine, show that uric acid, xanthine, sarcine, and guanine have the following constitution:—



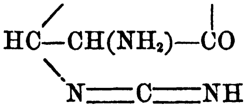
Uric acid.



Xanthine.

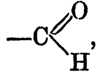
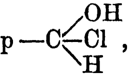


Sarcine (hypoxanthine).

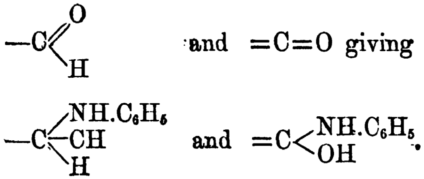


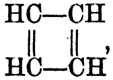
Guanine (amidosarcine).

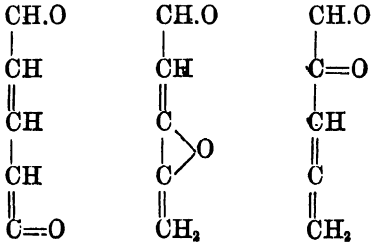
W. C. W.

Reaction of Urea with Furfurol. By HUGO SCHIFF (*Deut. Chem. Ges. Ber.*, x, 773—776).—Whereas most aldehydes easily react on aqueous or alcoholic solutions of urea, forming condensed ureas, furfurol appears to have no action upon such solutions. It acts, however, in a peculiar manner on solutions of urea nitrate, a violet colour being produced, which gradually disappears, with deposition of a black substance. The colour is not occasioned by the nitric acid. Aqueous solutions of furfurol are not coloured by dilute mineral acids, except after the furfurol has begun to decompose, when they certainly have this effect. Now although neither acid nor urea alone colours pure furfurol, yet a very characteristic change occurs when the two substances react together. If a solution of urea in about three parts of concentrated furfurol solution be treated with a few drops of concentrated hydrochloric acid, the liquid becomes warm, and then gradually of a splendid purple-violet colour, and finally solidifies to a solid brownish-black mass. This phenomenon takes place in alcoholic solutions. Aqueous furfurol solutions after some days, even if kept in the dark, acquire the property of becoming coloured by mineral acids. If hydrochloric acid of spec. grav. 1·10 be employed, a pale-red colour appears in about ten minutes, but if a small crystal of urea be dissolved in this solution, a deep violet colour is formed in a few minutes, slowly changing to brown and depositing a black substance. The reaction is very delicate, especially when conducted under the same conditions as a comparative test. The reaction was obtained with the slightly soluble polyureïds of the aldehydes. Urine gives the reaction. With many amides, as acetamide, benzamide, oxamide, sulpho-urea, mono- and diphenylthiocarbamide, taurine, glycocine, creatine, cyanuric acid, uric acid, alloxan, oxaluric acid, parabanic acid, the reaction is not obtainable; but it is obtained with allantoïn, though perhaps somewhat more tardily and less intensely than with urea. Setting out with the view that urea, a very soluble body, might favour the separation of water, and thus the formation of condensation-products, several very soluble salts were added to the furfurol solution, but no violet colour was occasioned. The hydrochloric acid acts in such a manner that the aldehyde group,  $-\mathrm{C}\begin{array}{l}/\!\!/\mathrm{O}\\ \diagdown\mathrm{H}\end{array}$, changes into the group  $-\mathrm{C}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{Cl}\\ \diagdown\mathrm{H}\end{array}$, which, having but little stability, acts easily on the amide-groups of the urea, water being separated, and hydrochloric acid re-produced, just as is the case in aldehyde-condensations effected by small quantities of hydrochloric acid, as formerly observed by the author. A result testifying in favour of such a primary reaction is observed when rather more hydrochloric acid is used, and the experiment is conducted as follows:—(The experiment is thus capable of the greatest delicacy.) A very small crystal of urea in a small dish is covered with a drop of highly concentrated aqueous furfurol solution, and a drop of hydrochloric acid of spec. grav. 1·10 is at once added. A change of colour occurs very rapidly through yellow, green, and blue into violet, the latter in a few minutes passing into a splendid purple-violet. This change of colour is quite different from that which altered furfurol-water would undergo without the addition of urea. The tint becomes so intense that in ten minutes the solution may be diluted with 50 to 80 times its bulk of water, and yet maintain its colour most definitely. The black substance separating in this latter case is amorphous, like carbon, and insoluble in ordinary solvents. Washed with water and dried at 110° it contains hydrogen and nitrogen. It is suspected to be a humus-like body, which has carried down some urea with it, to which it obstinately adheres. From the foregoing it is observed that furfurol behaves quite differently with urea and amides to what other aldehydes do. The difference of behaviour is observable in the case of basic amines. According to earlier researches by the author, aldehydes react with aniline and toluidine in such a manner that water separates and the diatomic aldehyde residue takes the place of the hydrogen of the NH_2— group: $C_6H_5{-}NH_2 + C_nH_mO = H_2O + C_6H_5{-}N{=}C_nH_m$, whilst, according to Stenhouse, two molecules of aniline or toluidine unite directly and without separation of water, with one molecule of furfurol to form basic bodies.

These compounds, likewise arising only on co-operation of acids, point to the presence of a second doubly combined oxygen-atom, so that two molecules of aniline could form two groups without water being taken up—



Nearly ten years ago the author sought to establish constitutional formulæ for the pyromucic acid group, just as Limpricht more recently has done in almost exactly the same manner, these compounds being regarded as derivatives of a diacetylene,  $\begin{matrix} HC{-}CH \\ \| \quad \| \\ HC{-}CH \end{matrix}$, just as the salicylic compounds are derived from benzene. This view is supported by the fact that furfurol resembles salicyl-aldehyde in many respects. The author is nevertheless of opinion that setting out from mucic acid and the polyanhydrides of glucose, it is possible to develop formulæ for furfurol, consisting of open chains, thus:—



W. S.

Furfurol. By ADOLF BAEYER (*Deut. Chem. Ges. Ber.*, x, 695—698 and 1358—1365).—In a previous communication (*Berichte*, x, 325: *Chem. Soc. Journ.*, 1877, 444) the author has shown that furfuracrylic acid on treatment with nascent hydrogen passes into furfuropropionic acid, the furfurol nucleus remaining unchanged. This nucleus does not however resist the action of oxidising agents, since according to Limpricht (*Liebig's Annalen,* clxv, 284) pyromucic acid, subjected to the regulated action of bromine, loses CO_2 and yields a body $C_4H_4O_3$, which by excess of bromine is changed into the mucobromic acid of Schmelz and Beilstein, $C_4H_2Br_2O_3$.

The author has now attempted, by the action of bromine in excess upon an aqueous solution of furfuropropionic acid, to obtain a body analogous to this mucobromic acid, but without success. He has therefore attempted a more limited oxidation of it.

Contrasting the formulæ of pyromucic and furfuropropionic acids, $C_4H_3O.CO_2H$ and $C_4H_3O.CH_2.CH_2.CO_2H$, it appeared probable that, if the development of CO_2 by the action of bromine upon the former acid depended on the destruction of the carboxyl group, the oxidation of the latter would take place without separation of CO_2. Experiment has confirmed this expectation, and also demonstrated that the evolution of CO_2 in the first case is really due to oxidation of the point of attachment in the molecule of the CO_2H group; for in this reaction four atoms of bromine are used, whereas *two* only are required for the oxidation of furfuropropionic acid.

When furfuropropionic acid in cold aqueous solution is treated with exactly one molecule of bromine, and the solution extracted with ether, a body is obtained which in all probability is the analogue of Limpricht's $C_4H_4O_3$. On account of its instability, the author did not attempt its purification, but at once treated the bromine mixture with 3 molecules of silver oxide, whereby a reaction was obtained corresponding with the equation—

$$C_7H_8O_3 + Br_2 + H_2O + 3Ag_2O = C_7H_6Ag_2O_5 + 2AgBr + 2H_2O + Ag_2.$$

When the reaction was terminated, a sufficiency of hydrochloric acid was added, and by shaking with ether the resulting mass, a bibasic acid, *furonic acid,* $C_7H_8O_5$, was obtained in colourless needles, melting at 180°. These are sparingly soluble in cold water and in ether.

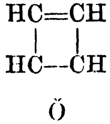
By the action of sodium amalgam in the cold, or by heating with hydriodic acid and amorphous phosphorus to 160°, furonic acid passes into *hydrofuronic acid,* $C_7H_{10}O_5$. This acid, which is very soluble in water, crystallises in colourless needles fusing at 112°.

Heated with hydriodic acid and red phosphorus to 200—205°, furonic acid yields, in addition to an oily body which is probably caproic acid, crystals of a bibasic acid having the composition $C_7H_{12}O_4$. The identity of this acid with α-pimelic acid obtained by Schorlemmer and Dale (*Deut. Chem. Ges. Ber.*, vii, 808) from suberone, was established by a careful comparison of their properties. From this it follows that furonic acid belongs to the normal series.

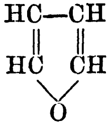
On boiling with baryta-water, furonic acid gives a yellow precipitate, possessing all the properties of the baryta-compound of fumaric aldehyde described by Limpricht.

Constitution of the Furfurol-group.—The author proposes for the group C_4H_4O (Limpricht's *Tetraphenol*) the name "furfuran." Since this furfuran is not affected by sodium or sodium-amalgam, it cannot have the constitution of an aldehyde, ketone, alcohol, or ordinary ether. Of known types, then, it can belong only to that of ethylene oxide. Possibly it might be represented on the type of the unknown vinyl-ether, $CH_2{=}CH.OCH{=}CH_2$]. The first hypothesis leads to formula (1), the second to (2) or (3).

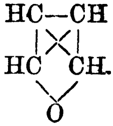
(1.)



(2.)



(3.)



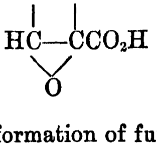
All three formulæ are in harmony with Malaguti's observation that pyromucic ether unites directly with 4 atoms of chlorine.

Limpricht has lately observed that pyromucic acid when acted upon by 4 atoms of bromine yields CO_2 and $C_4H_4O_3$:

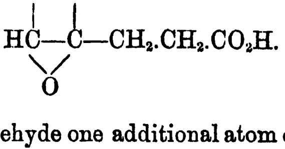
$$C_5H_4O_3 + 4Br + 2H_2O = CO_2 + C_4H_4O_3 + 4HBr.$$

Inasmuch as this body yields by oxidation fumaric acid, Limpricht regards it as the aldehyde of that acid. Omitting its separation, the author, by treating the product of the above reaction with silver oxide, has also obtained fumaric acid, but in such small quantity as to show that the reaction is by no means so simple as it at first sight appears; and he remarks that if the body $C_4H_4O_3$ is really the aldehyde of fumaric acid, analogy would lead us to expect the formation from it, by the action of bromine in excess, of an aldehyde of dibromosuccinic acid; whereas it yields a substitution product, namely, mucobromic acid.

Independently of these considerations, if it be admitted that the splitting of the chain of nuclear carbon atoms on oxidation of pyromucic acid, takes place at the locus of the oxygen, formula (1) most easily explains the formation of fumaric acid. The position of the side-chain in pyromucic acid and in the furfuro-propionic acid formed from its aldehyde, is then determined by the oxidation of the latter, which yields α-pimelic acid, a *normal* compound. Hence these acids must have the constitution—



and



For the formation of furonic aldehyde one additional atom of oxygen is necessary, the one already present forming with one of the parted carbon atoms an aldehyde-group, while that which enters unites with the other to form a ketone group, which remains joined with the side-chain—

$$COH.CH{=}CH.CO.CH_2.CH_2.CO_2H.$$

The aldehyde, by oxidation, changes into furonic acid,

$$CO_2H.CH{=}CH.CO.CH_2.CH_2.CO_2H,$$

and this by reduction yields, as a final product, normal pimelic acid—

$$CO_2H.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H.$$

The intermediate products have not yet been investigated. On the other hand, when pyromucic acid is oxidised to fumaric aldehyde, 2 atoms of oxygen (= 4 atoms bromine) are necessary, since not only is CO_2 split off, but the carbon atom to which it was united is oxidised to a carboxyl group, giving an aldehyde of fumaric acid,

$$COH.CH{=}CH.CO_2H.$$

Ch. B.

Furfurangelic Acid and Furfurobutylene. By ADOLF BAEYER and P. TÖNNIES (*Deut. Chem. Ges. Ber.*, x, 1364—1365).—When furfurol, normal butyric anhydride and sodium butyrate are heated gradually for 12 hours from 100° to 180°, and the resulting mass is dissolved in soda-solution, and treated with sulphuric acid, a considerable quantity of *furfurangelic acid*, $C_4H_3O.CH{=}CH.CH_2.CH_2.CO_2H$, is separated. The acid crystallises from hot water in colourless silky needles, which melt at 87—88°. Sodium amalgam reduces it easily to normal *furfurovaleric acid*, $C_4H_3O.CH_2.CH_2.CH_2.CH_2.CO_2H$, a colourless oil, which gives a crystalline acid on treatment with silver oxide.

Isobutyric anhydride, potassic isobutyrate and furfurol behave differently. The reaction, accompanied by copious evolution of CO_2, begins at 70°, is energetic at higher temperatures, and is complete after four hours at 150°. A very small quantity of a crystalline acid is obtained, the principal product being an oil insoluble in potash, which has the composition of *furfurobutylene*,

$$C_4H_3O.CH = CH.CH_2.CH_3.$$

It boils at 153°, and smells like *Carabus sycophanta*.

It is the second known hydrocarbon derivative of furfuran, the first being a body obtained by Cahours from thio-furfurol, and consisting, according to Schwanert's analyses, of the stilbene of furfuran,

$$C_4H_3O.CH{=}CH.C_4H_3O.$$

Both are under examination. Ch. B.

Some Products of the Distillation of Wood at Low Temperatures. By H. B. HEILL (*Deut. Chem. Ges. Ber.*, x, 936—939).—The author paid a visit to a wood-vinegar factory in Brooklyn, in which the wood was distilled at a carefully maintained temperature below 200°. He observed that in the rectification of the crude products, a heavy oil but slightly soluble in water, went over with the steam. The oil freshly obtained, was reddish-yellow, and of peculiar odour. Dried over calcium chloride and distilled, it began to boil at 100°, the thermometer quickly rising to 160°, and remaining between 160° and 170°, when the greater part came over: it then quickly rose to 200°.

By repeatedly fractionating, 60 per cent. of an oil was at last obtained, distilling between 160—165°. Most of it passed over at 162°. The almost colourless, strongly refractive liquid, smelling of bitter almond oil, was easily recognised as furfurol.

The occurrence of furfurol amongst the products of the distillation of wood is not new. Völkel has found it in small quantities in crude wood-vinegar. The author is not in the position to give the quantity of furfurol formed at these low temperatures, but says it must be considerable in order to separate out spontaneously from the aqueous distillate, as it does.

The crude oil shaken with dilute soda solution, assumes a deep yellow colour, becomes turbid, and on standing for a long time, deposits a yellow precipitate, which crystallises from alcohol in beautiful needles. An attempt was made to separate this body by distillation, but without success, as this means is insufficient to separate it from the furfurol. It was found impossible also to separate the furfurol by means of sodium bisulphite solution, or other solvents.

To prepare this yellow body in the pure state, it was found best first to free the crude oil partially from the high-boiling portions. The distillate coming over under 175°, and consisting of nearly 85 per cent. of the oil employed, is shaken with soda-solution (1 : 4), and the whole cooled down. After a short time it is separated from the lye, washed with a little water, and distilled with steam. A red oil is left in the retort, which mostly solidifies on cooling. This residue treated with cold alcohol, gives up to this solvent the red oil arising from the decomposition of the furfurol, and crystals of the yellow body are left behind, which were re-crystallised from boiling alcohol. The properties of the body are as follows:—Long, orange-yellow needles, which melt at 162°, and volatilise, but not without decomposition at a higher temperature. Easily sublimed in a slow stream of air. Insoluble in potash. Soluble in sulphuric acid with splendid purple colour, in concentrated hydrochloric acid with purple-red, and in acetic acid with yellow colour. Soluble with some difficulty in ether and carbon bisulphide; insoluble in cold, easily soluble in hot alcohol. Apparently unaltered by reducing agents. There can scarcely be a doubt that this body is the pyroxanthine discovered by Scanlan, and more closely investigated by Gregory and Apjohn. A combustion gave results agreeing very nearly with those obtained by Gregory and Apjohn. In the soda-lye separated from the furfurol were found pyromucic acid, and a small quantity of an oil not yet investigated, and smelling strongly like smoke-dried fish. It distilled over easily with steam.

W. S.

On Benzene Formulæ. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1154—1155).—This is a criticism on a notice by van't Hoff with regard to the prismatic formula, in which the author points out that the error which van't Hoff has fallen into of there being two ortho and two meta derivatives possible, is due to his considering the position of the atoms in space and not merely with reference to their mode of connection. C. E. G.

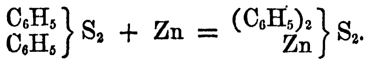
The Oxychlorination of Benzene. By F. KRAFFT (*Deut. Chem. Ges. Ber.*, x, 797—800).—Carius obtained trichlorophenomalic acid by the action of potassium chlorate and dilute sulphuric acid on benzene, and it is regarded as a substance homologous with malic acid. As this body with its reactions belongs to that part of organic chemistry which contains debateable ground, the author determined upon a revision of Carius' statements. This determination was in part carried out. Pure benzene was used for preparing the trichlorophenomalic acid. The deep shades of colour produced in the benzene by the action of very small quantities of potassium chlorate were very striking, but these shades quickly disappeared in the course of the reaction. The reaction runs to a great extent in the direction of forming trichlorophenomalic acid, but the presence of syrupy bodies occasions a considerable loss of substance. The yield of pure product does not amount to more than 3 to 4 per cent. of the benzene employed. A portion of this benzene itself is lost by evaporation.

The following physical properties of trichlorophenomalic acid were observed, and they agree with Carius' observations. This body dissolves with difficulty in cold water, but easily in boiling water, in which it usually melts to a colourless oil before dissolving. Incompletely saturated hot solutions show evidences of supersaturation on cooling. The solution when left at rest deposits crystals only after a long time, but on agitating or introducing a fragment of a crystal, it becomes a pasty mass of minute, colourless, shining plates or needles. The body is easily soluble in the cold in alcohol, ether, and benzene. Once or twice recrystallised from boiling water, in the vapour of which it is tolerably volatile, it had a melting point of 131—132°. (Carius.) At higher temperatures it volatilised without change. The author obtained 133—134° as the melting point. Heated in a fine capillary tube for some minutes to 200° the trichlorophenomalic acid acquired a brown colour and diffused the odour of chloranil. The product melting at 131—132°, whose properties agreed well with those given by Carius, was analysed. The chlorine determinations were made with a substance dried in the exsiccator, whereas Carius dried his substance at 100°, and hence lost crystallisation-water. There was thus a difference of about 8 per cent. in Carius' and the author's results as regards the chlorine. Altogether the total results were found to agree very well with the empirical composition of trichlorhydroquinone, ($C_6Cl_3H_3O_2$). The great difficulty in purifying the body is quite in accordance with the remarks of Graebe with respect to tetrachlorhydroquinone. In fact the description of trichlorophenomalic acid by Carius is an almost exact repetition of what was said a long time ago by Städeler, and more recently by Graebe, about trichlorhydroquinone. The trichlorophenomalic acid, in hot aqueous solution was now oxidised with nitric acid (fuming). Nitrogen escaped, and delicate yellow plates with the properties of trichloroquinone were obtained. Melting point 165—166°. According to a statement of

Carius, "The layer which floats on the acid solution of the trichlorophenomalic acid, during this preparation, contains a chlorine compound, scarcely soluble in water, and crystallising in delicate yellow plates." This benzene solution, forming the layer alluded to, was collected and evaporated on the water-bath. On cooling, golden-yellow crystals separated abundantly, mixed with a thick syrup. On addition of alcohol the syrup dissolved, leaving the crystals undissolved. These consisted of a mixture of small plates and thick prisms, the former of which easily dissolved in cold alcohol, whilst the prisms remained. Analysis showed a very near agreement with the numbers required for trichloroquinone, $C_6Cl_3(HO)_2$. The substance melted at 165—166°, and sublimed below this temperature without alteration. Dilute potash first coloured it green, and then dissolved it with reddish-brown colour, and the liquid on standing deposited the characteristic needles of potassium chloranilate. Sulphurous acid in aqueous solution, especially on warming, converted it into trichlorhydroquinone. The body which crystallised in thick prisms from the benzene solution forming the supernatant layer above alluded to, dissolves with great difficulty in cold, and by no means easily, in boiling alcohol. It is thus easily purified. According to analysis this body is dichloroquinone, and it appears to be isomeric with that of Faust. Its melting point (164°) does not differ greatly from that of trichloroquinone. The difference on the contrary is great between the dichlorhydroquinone, obtained from dichloroquinone by reduction with sulphurous acid and trichlorhydroquinone. On boiling the dichloroquinone with sulphurous acid it dissolves, giving a violet-black and then blood-red coloration, especially noticeable at first; with insufficient quantity of reducing agent, a colourless solution is finally obtained. This solution deposits slender shining needles soluble with difficulty in cold water. Melting point = 172°. Analysis proved it to be pure dichlorhydroquinone, $C_6Cl_2H_4O_2$. The direct formation of a phenol-like body (trichlorhydroquinone) from benzene by a process of oxidation running through different phases is deserving of notice from many points of view. First, as in the present case, there is proof that an immediate phenol-formation from aromatic hydrocarbons may, under certain conditions, take place, and especially where the previous entrance of electro-negative chlorine makes the supply of oxygen difficult. It is at the same time settled that the formation of trichloroquinone, as already hypothetically assumed by many chemists, precedes that of the trichlorohydroquinone; and it is not considered a too venturesome generalisation to assume that in other processes of oxidation also, the formation of quinones, ketones, and aldehydes precedes that of the corresponding hydro-compounds, which latter, under the conditions of the reaction, are mostly unstable, and can be isolated only in exceptional cases. W. S.

Preparation of Benzene Hydrosulphide from Benzene-sulphinic Acid. New Method of converting Benzene Disulphide into Benzene Hydrosulphide. By R. OTTO (*Deut. Chem. Ges. Ber.*, x, 939—941).—Voigt's method for the preparation of benzene hydrosulphide by the reduction of the chloranhydrides of benzene sulphonic acid by means of zinc and dilute sulphuric acid gives only a moderate yield. It is not only the insolubility of the chloranhydride which stands in the way, thus making it difficult of access to the nascent hydrogen, but a portion of the undecomposed compound is withdrawn during the distillation from the reducing action, and converted into benzenesulphonic acid, which is not converted into hydrosulphide by nascent hydrogen.

The author and Schiller found that the chloranhydride of the benzenesulphonic acid could be easily converted into the zinc salt of the sulphinic acid (zinc benzenesulphite) by the action of zinc-dust. It was then proposed to prepare the hydrosulphide from this salt, or from the sodium salt prepared from it. The crude zinc salt (*i.e.*, the zinc benzenesulphinate) is to be added gradually to a mixture of zinc and hydrochloric acid which is gently giving off hydrogen, and the whole is cooled. The action is continued until all the sulphinic acid is converted into hydrosulphide and disulphide. A small quantity of the clear liquid taken out and examined will then redden blue litmus-paper, and when acted upon by a bit of zinc, will yield no more hydrosulphide (tested by the smell and action on a strip of lead-paper). As regards the formation of benzene disulphide, it is found that the hydrosulphide at ordinary temperatures has a great inclination, in presence of the sulphinic acid, to become changed to disulphide with liberation of water. This disulphide in neutral solution, treated with zinc in a finely divided state and gently warmed, is completely converted, after a short time, into the zinc salt of the hydrosulphide, thus:—



$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}S_2 + Zn = \left.\begin{matrix}(C_6H_5)_2\\Zn\end{matrix}\right\}S_2.$$

Zinc salt of hydrosulphide.

In the above-mentioned method of preparation, if care be not taken to cool the liquid, loss will result, part of the benzenesulphinic acid being split up into benzene disulphoxide and irreducible benzenesulphonic acid, thus:—

$$3C_6H_6SO_2 = C_{12}H_{10}S_2O_2 + C_6H_6SO_3 + H_2O.$$

(Benzene sulphinic acid is easily decomposed according to this equation by boiling with water.)

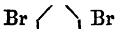
To the solution tested with litmus-paper, &c., containing little free acid, zinc-dust is added in excess, and warmth is applied to further the formation of the zinc compound of the hydrosulphide. Acid is again added (hydrochloric acid), and the hydrosulphide finally distils over with the vapour of water. By attention to the directions, an excellent yield is obtained. As might be expected, this new method of converting benzene disulphide into benzene hydrosulphide by means of zinc-dust will be of universal applicability, and will also permit the conversion of halogen-substituted disulphides (which are not reducible by nascent hydrogen without substitution of halogen by hydrogen) into the corresponding hydrosulphides. The author has employed the method for preparing paratoluene hydrosulphide.

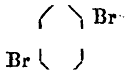
By the action of compact or granulated zinc, only traces of benzene disulphide are converted into the zinc-compound of the hydrosulphide.

W. S.

Preparation of Durene from Paradibromo-benzene. By PAUL JANNASCH (*Deut. Chem. Ges. Ber.*, x, 1354—1357). By heating together for some time, by means of a paraffin-bath at 160—170°, a benzene solution of dibromo-paraxylene, methyl iodide, and sodium, the author has obtained durene (tetramethyl-benzene) together with a little pseudocumene. Dibromo-paraxylene is prepared by the action of bromine in presence of iodine upon paraxylene, which again is most easily formed synthetically from dibromo-benzene by the action of methyl iodide and sodium. Full particulars of the process are given.

Two years ago the author obtained, by the action of methyl iodide and sodium upon monobromo-mesitylene, a compound which he has named β-tetramethylbenzene (*Deut. Chem. Ges. Ber.*, viii, 355). Durene being an isomeride of this body, it follows that the dibromoparaxylene, from which it is prepared—





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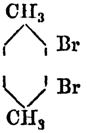
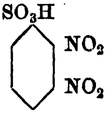
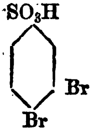


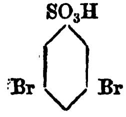
can only have the constitution (2) or (3), since the dibromoxylene of constitution (1) must yield β-tetramethylbenzene. Mesitylene is here assumed to be symmetrical trimethyl-benzene.

The author purposes studying the derivatives of β-tetramethyl-benzene, as well as those of the isomeric paradiethyl-benzene, which he hopes to obtain by the action of ethylbromide and sodium upon dibromobenzene.

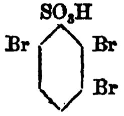
Ch. B.

Dinitrobenzeensulphonic Acid. By A. SACHSE (*Liebig's Annalen*, clxxxviii, 143—157).—Metanitrobenzenesulphonic acid, prepared from benzene, was separated from the ortho- and para-acids by crystallisation of the calcium salt, regeneration of the acid by means of alcohol and sulphuric acid, and finally by recrystallisation of the barium salt and regeneration by sulphuric acid. By treating this acid with sulphuric and fuming nitric acids the dinitro-acid  is formed, together with some dinitrophenol. This dinitro-acid is converted into barium salt and crystallised. The free acid is a brownish syrup solidifying to a crystalline mass on cooling; it is very soluble in alcohol and highly deliquescent. The ammonium salt (anhydrous), the potassium salt (containing $1\frac{1}{2}H_2O$), and the barium and lead salts (containing $3H_2O$) were prepared and examined. The chloride melted at 89° (Limpricht found 97°), and the amide at 283° (235°, Limpricht). Reducing agents gave rise to *diamidobenzenesulphonic acid*, $C_6H_3\left\{\begin{matrix}(NH_2)_2\\ SO_3H\end{matrix}\right. + 1\frac{1}{2}H_2O$, a well-marked acid, although it combines with hydrochloric, hydrobromic, sulphuric acids, &c., to form crystallised salts; it also forms a stannosochloride. By conversion into diazo-derivative and treatment with hydrobromic acid, it yields *dibromobenzenesulphonic acid*, of which the potassium salt is anhydrous; the barium and lead salts crystallise with $3H_2O$ and the calcium salt with $2H_2O$; the chloride melts at 127° and the amide at 215° (with browning). Since there are but four possible dibromobenzenesulphonic acids obtainable from *meta*-nitrobenzenesulphonic acid, and three of them are already known, viz.:—

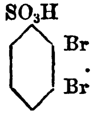




and



the chlorides of which melt respectively at 34°, 57·5°, and 71°, and the amides at 175°, 203, and 193°, it follows that the acid must be the fourth modification,



C. R. A. W.

Condensation in the Ortho Series. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1123—1131).—4. *Tolylenediamine and Formic Acid.*—When equal parts of orthotolylenediaminic (m. p. 89°) and formic acid are digested together for some time, and the product is distilled, an oil of high boiling point is obtained which becomes crystalline after a time. These crystals could not be obtained in a pure state, but a solution of them in hydrochloric acid yielded with platinum tetrachloride a yellow precipitate, which, after being crystallised from boiling water, was found to have the composition $(C_8H_8N_2HCl)_2.PtCl_4$. The base therefore has the composition, $C_8H_8N_2$, and is *methenyltolylenediamine:* its formation may be thus represented, $C_7H_6(NH_2)_2 + CH_2O_2 = C_7H_6N_2H.CH + 2H_2O$. It melts at 98—101°.

5. *Orthoamidophenyl and Formic Acid.*—Equal parts of these two compounds when digested together and subsequently distilled yield, above 150°, a colourless oil of high refractive power, which after being freed from formic acid by means of potassium carbonate solidifies to a mass of crystals. This substance may be purified by repeated rectification when it boils at 182·5°, and the crystals fuse at 30·5°. It has the composition of *methenylamidophenol*, C_7H_5NO, and is formed thus: $C_6H_4(NH_2).OH + CH_2O_2 = C_6H_4NO.CH + 2H_2O$. The crystals appear to be monoclinic prisms. They are only slowly acted on by water, but are easily decomposed when heated with concentrated hydrochloric

acid: on cooling the solution solidifies to a mass of crystals consisting of amidophenol hydrochloride.

6. *Orthoamidophenol and Oxalic Acid.*—These two substances when heated together until gas ceases to be evolved, yield a dark-coloured product, from which colourless needles were obtained by repeated crystallisation from alcohol. Their examination is not yet completed.

7. *Orthotolylenediamine and Phthalic Anhydride.*—The product obtained on heating one part of the diamine with two of the anhydride until water ceased to be given off and it fused quietly, was powdered when cold and treated with a warm solution of potassic carbonate. The residue, on repeated crystallisation from dry acetic acid yielded thick lustrous yellowish prisms of *diphthalyltolylenediamine*, $C_{23}H_{14}N_2O_4$ or $C_7H_6(NC_8H_4O_2)_2$, corresponding with phthalanil, $C_6H_5.NC_8H_4O_2$. It melts at 270°, and is but slightly soluble in most solvents; attempts to obtain condensation-products from this substance by removal of CO_2 failed.

8. *Orthotolylenediamine and Benzoic Aldehyde.*—On mixing one part of the former with two of the latter heat is evolved, and the mixture on being heated for several hours at 180° gives off water. The product exhausted with hot dilute hydrochloric acid yields a solution which on cooling deposits *dibenzyltolylenediamine hydrochloride* in an impure state. By repeated crystallisation from dilute acid with aid of animal charcoal it is obtained in colourless needles. The free base, $C_{21}H_{18}N_2$, may be obtained by decomposing the salt with ammonia; it crystallises from alcohol in transparent lustrous prisms, which melt at 188—191°, and are almost insoluble in water. It is easily soluble in alcohol, especially when warm, and in dilute acids. The platinum salt is almost insoluble in water and hydrochloric acid, but crystallises from alcohol in nodules which have the formula $(C_{21}H_{18}N_2HCl)_2.PtCl_4$.

Tolylenediamine appears to form condensation-products with other aldehydes; the author has obtained such a base with salicylic aldehyde which he is at present investigating.

The object with which the examination of condensation-products in the ortho series was originally undertaken, was the synthesis of indigo, and the following are some of the experiments made in that direction. When an aqueous solution of orthotoluidine hydrochloride is mixed with ferric chloride and left at rest, blue flocks are deposited which gradually increase in number. After 24 hours these were collected and washed successively with hot dilute hydrochloric acid, dilute soda-solution, hot water, and alcohol. The violet-blue powder thus obtained is insoluble in ordinary solvents, and is free from chlorine: in contact with hydrochloric acid it becomes greenish, probably from formation of a hydrochloride, as the blue colour is restored by alkalis. It dissolves in aniline with a magnificent blue colour, and dyes silk and wool blue. This toluidine-blue differs from indigo in that it cannot be volatilised without decomposition, and it cannot be reduced and reoxidised moreover, although it dissolves in sulphuric acid with a blue colour, the solution when diluted soon becomes colourless. The analyses that have hitherto been made of this substance are not concordant, which is accounted for by the difficulty of purifying it. This reaction would seem to be characteristic of the ortho series, as paratoluidine under similar treatment does not yield a trace of a blue precipitate. The reaction which takes place with aniline, the author believes to be due to the presence of pseudotoluidine, or to be connected with the formation of aniline black.

Formorthotoluide.—A compound having the composition of formorthotoluide was prepared by distilling a mixture of equal parts of oxalic acid and orthotoluidine, and crystallising the distillate from alcohol, or better by merely heating the mixture until gas ceased to be evolved, and after cooling and pulverisation, extracting it with alcohol, ether, and dilute hydrochloric acid, and finally crystallising it from toluene or dry acetic acid. It forms colourless needles of the formula, $C_7H_7NH.CHO$, which melt at 211°, and are almost insoluble in ether and in cold alcohol. An investigation of this substance soon showed that it was not the true formorthotoluide, which may be obtained by the action of formic acid on orthotoluidine; for the present, the author proposes to call it isoformorthotoluide. When orthotoluidine and formic acid in molecular proportions are digested for some hours and then distilled, a liquid passes over between 278° and 292°, which solidifies on standing, and on repeated rectification may be obtained of constant boiling point, 288°. The crystals are purified by pressure, washing with dilute hydrochloric acid, and crystallisation from alcohol, in which they are easily soluble. They are large tables which melt at 56·5—57·5°. This compound, the true formorthotoluide, is resolved into formic acid and orthotoluidine, when boiled with dilute sulphuric acid, whilst the isomeric body remains unchanged even at 150°. Formorthotoluidine, when distilled with phosphoric anhydride, or when heated alone at 300°, yields orthotoluidine, but in the latter case another compound is formed in small quantity. It may be more conveniently prepared by digesting the formotoluide for a long time at the boiling temperature, and then distilling off the toluidine and unaltered toluide until the thermometer indicates 300°. The residue crystallised successively from alcohol and from toluene, yields the new substance in colourless glistening prisms which melt at 153°. It dissolves with difficulty in boiling alcohol, easily in hot toluene. The analyses agree with the formula, C_8H_9N, the other products of the reaction being toluidine, CO and CO_2—

$$2(C_7H_7NH.CHO) = C_9H_9N + C_7H_7.NH_2 + CO_2$$
$$C_7H_7NH.CHO = C_7H_7NH_2 + CO.$$

The constitution of the body C_8H_9N is not yet known, but the author remarks that it has a composition intermediate between that of methyltoluidine and indol; it dissolves in hydrochloric acid, yields toluquinone on oxidation, and appears to form an addition-product with bromine. Formorthotoluide and orthamidoethylbenzene hydrochloride yield blue compounds when treated with ferric chloride, whilst the body C_8H_9N is but slowly altered, and isoformorthotoluide is not acted on at all. The author finds that indol treated with ferric chloride yields a greenish-grey substance soluble in aniline with a brown colour: it is not volatile. C. E. G.

On Ammonium Compounds. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1152—1153).—This is a reply to Meyer's objection that the compounds $N(C_2H_5)_3.C_7H_7I$ and $NC_7H_7(C_2H_5)_2.C_2H_5I$ obtained by the author, are one and the same compound, the slight differences observed being due to a small quantity of resin or like impurity. The author states that when triethylbenzylammonium chloride is converted into the corresponding iodide by means of silver oxide and hydriodic acid, and the neutral solution concentrated on the water-bath, a clear solution is obtained which gives off benzyl iodide on boiling with concentrated hydriodic acid. If, however, the clear solution is evaporated under an exsiccator, it solidifies to a crystalline mass, which no longer gives benzyl iodide when heated with hydriodic acid. From this the author infers that the compound undergoes isomeric change when evaporated to dryness. C. E. G.

Monomethylaniline. By E. NÖLTING and J. B. BOASSON (*Deut. Chem. Ges. Ber.*, x, 795—796).—Kern declares that he has been unable to prepare monomethylaniline from either methyl alcohol and aniline chloride, or methyl iodide and aniline. Hepp also failed to obtain monomethylaniline according to the latter method. These facts not harmonising with the earlier observations of Hofmann, Girard and De Laire, &c., the authors determined to put the matter to a practical test. They found that monomethylaniline is abundantly formed in both reactions. In order to separate the secondary amine from the product of the reaction, which contains at the same time unaltered aniline and dimethylaniline, use was made of nitrous acid. Sodium nitrite was in fact added to a not too concentrated acid solution of the bases, which was well cooled. Thus, aniline is converted into diazobenzene-chloride, dimethylaniline into nitrosodimethylaniline chloride, which remains in solution, whilst the methylphenylnitrosamine formed at the same time is separated as a yellow oil, which can be extracted from the solution by means of ether. By reducing agents (tin and hydrochloric acid, or iron and acetic acid) monomethylaniline is easily obtained, and with quantitative exactness. This body was dissolved by sulphuric acid, forming an absolutely clear solution. It distilled over almost completely between 190—192°, gave with chloride of acetyl the acetyl-derivative described by Hofmann and Hepp, and when treated in acid solution with sodium nitrite, nitrosamine. The platino-chloride, precipitated from the hydrochloric acid solution by platinum tetrachloride, gave without further purifying, correct numbers on analysis. The following numbers testify to the fact that the yield of monomethylaniline is considerable.

(1.) 50 grams of mixed bases obtained by the action of 1 mol. of methyl iodide on 1 mol. of aniline, yielded 21 grams of the dry nitrosamine, corresponding to 16·5 grams of methylaniline.

(2.) 50 grams mixed bases, obtained by the action of 1 mol. of methyl iodide on 2 mols. of aniline, and separated from the crystals of the aniline iodide by means of ether, yielded 23·5 grams of nitrosamine, corresponding to 18·5 grams of methylaniline.

(3.) The product of the reaction of 25 grams of methyl alcohol on 100 grams of aniline chloride at 235—240°, gave 41 grams of nitrosamine, corresponding to 32·3 grams of methyl aniline. There is no doubt that in the preparation of dimethylaniline in quantity, monomethylaniline may be formed also. In two samples of commercial dimethylaniline the presence of small quantities of monomethylaniline was detected by the formation of nitrosamine, and in like manner some commercial diethylaniline yielded a small quantity of ethylphenylnitrosamine. The reaction is very delicate. Artificial mixtures were prepared of absolutely pure dimethyl- and monomethylaniline, and it was then found that one per cent. of the latter could be detected with certainty. One gram of the bases was dissolved in excess of tolerably dilute hydrochloric acid, a couple of drops of sodium nitrite solution added, the whole shaken with ether, and the ethereal extract was dried with calcium chloride, and evaporated on a watch glass. The methylphenylnitrosamine remains behind in yellow drops, and is recognised by a characteristic odour, and by means of Liebermann's reaction. Pure dimethylaniline leaves no oily drops, but a trace of a yellow crystalline body, probably nitrosodimethylaniline chloride, of which a small quantity might have been taken up by the ether. With the nitrosamine this body cannot be confounded. Probably this nitrosamine reaction will give rise to a method of quantitative estimation of the monomethylaniline contained in commercial methylaniline.

W. S.

Nitro-derivatives of Diphenylamine. By P. T. AUSTEN (*Amer. Jour. Sci.* [3], xiii, 279).—Pisani (*Ann. Chem. Pharm.*, xcii, 326) found that trinitrochlorobenzene acts on ammonia with formation of trinitraniline. Clemm (*J. pr. Chem.* [2], i, 145) obtained trinitrodiphenylamine by using aniline in place of ammonia, and a dinitrodiphenylamine by the action of dinitrobromobenzene on aniline.

The trinitrochlorobenzene was made in the following manner. 100 grams of picric acid were well mixed with 200 grams of phosphorus pentachloride in a flask with reversed condenser. On applying a gentle heat the mixture fused, and the reaction took place violently and without further heating. After the action had ceased, most of the phosphorus oxychloride was distilled off. The heavy red liquid remaining in the retort was then poured into a large quantity of cold water and violently agitated. The impure substance thus obtained was purified by washing with ether and crystallisation from absolute alcohol. It then formed bright yellow crystals, becoming darker on drying. The yield is from 30—40 per cent. of the theoretical amount.

Better results were obtained by simply heating the substances in a tall beaker, and by using half the previous quantities. The trinitrochlorobenzene thus obtained fused at 82·5—83°.

α-Trinitrophenylmetanitraniline, $C_{12}H_7N_5O_8$
$= NH[C_6H_4(NO_2).C_6H_2(NO_2)_3]$.—
25 grams of metanitraniline and 27 grams of chloropicryl were dissolved in boiling absolute alcohol; after a few minutes' boiling a heavy yellow crystalline sand began to separate. The solution was allowed to cool, and the precipitate was separated by filtration, and crystallised from glacial acetic acid. The formation of this compound is expressed by the following equation:—

$$C_6H_2(NO_2)_3Cl + 2C_6H_4(NO_2)NH_2 = NH[C_6H_4(NO_2)][C_6H_2(NO_2)_3] + C_6H_4(NO_2)NH_2.HCl.$$

α-Trinitrophenylmetanitraniline is almost insoluble in hot water, colouring it yellow, however; nearly insoluble in boiling ether, carbon disulphide, carbon tetrachloride, chloroform, and absolute alcohol; insoluble in hydrochloric and dilute nitric and sulphuric acids; easily soluble in strong sulphuric acid with deep wine-red colour, separating unchanged on addition of water; easily soluble in aniline, with red colour; also in hot amyl alcohol, but crystallises badly therefrom; soluble in hot glacial acetic acid, and separates on cooling as an orange crystalline sand. From acetyl chloride it separates in small wine-yellow transparent crystals.

Aqueous ammonia dissolves it very easily, the solution attaining a splendid scarlet colour. By evaporation it separates unchanged. With weak solutions of the alkalis it behaves as with ammonia; concentrated solutions, especially on heating, decompose it, with evolution of ammonia.

The compound consists of a heavy, crystalline, yellow sand, melting at 205° to a red liquid, which solidifies at about 175°. By careful heating it volatilises as a yellow powder. When thrown on a hot surface it explodes like gunpowder, but it is not exploded by percussion.

α-Trinitrophenylparanitraniline, $C_{12}H_7N_5O_8 = NH[C_6H_4(NO_2)][C_6H_2(NO_2)_3]$.— This compound was made in a manner similar to the preceding. Paranitraniline, with the calculated amount of picryl chloride, was dissolved in absolute alcohol; on boiling, a red crystalline powder separated, which was washed, and crystallised from glacial acetic acid. It melts at 216°, and resembles in solubility the preceding compound. In aqueous ammonia it dissolves easily, with red colour, and is reprecipitated unchanged by acids. From alcoholic ammonia it crystallises in beautiful glittering leaves. It dissolves in a hot solution of sodium carbonate, with scarlet colour; on cooling, violet needles separate, which are doubtless the sodium salt of α-picrylparanitraniline, $NNa[C_6H_4(NO_2)][C_6H_2(NO_2)_3]$. The needles are soluble in water and alcohol, and are decomposed by acids.

The trinitro-base is insoluble in aqueous ammonium carbonate, easily soluble in amyl alcohol, and crystallises therefrom in glittering yellow scales. In aniline it dissolves easily, and separates on evaporation in a crystalline form; dissolves also in benzoyl chloride, acetyl chloride, benzyl chloride, and chlorobenzene.

Dinitrophenylmetanitraniline, $C_{12}H_8N_4O_6, = NH[C_6H_4(NO_2)][C_6H_3(NO_2)_2]$.— Calculated amounts of dinitrobromobenzene (produced by nitration of bromobenzene) and metanitraniline were rubbed to a pulp with absolute alcohol, and the mixture heated to 100° for twenty hours in a sealed tube. On cooling, the tube contained hard brown crystals, which were washed with warm alcohol and crystallised from glacial acetic acid.

The substance is insoluble in water, alcohol, and ether, difficultly soluble in boiling glacial acetic acid, soluble in an excess of boiling chloroform, and separates on cooling in small yellow crystals, melting at 189°,* to a red liquid. With alkalis it behaves in the same manner as trinitrophenylparanitraniline.

Dinitrophenylparanitraniline, $C_{12}H_8N_4O_6$
$= NH[C_6H_4(NO_2)][C_6H_3(NO_2)_2]$.—
The calculated quantities of dinitrobromobenzene and paranitraniline were treated as in the preparation of the preceding compound. On cooling, the tube contained a mass of dark-red crystals. They were washed with dilute alcohol, and purified by precipitation with water from their acetic acid solution. The substance is *easily soluble in cold glacial acetic acid*, thus showing a marked difference from the *meta*-compound, which is *difficultly soluble in boiling glacial acetic acid*. It is difficultly soluble in cold alcohol, easily in hot. It is a very light, pale yellow, elastic, and electric powder. Melting point 181°.

Since the picrylnitranilines contain the mononitrophenyl group, it appears extremely probable that a further nitration can be effected. In this case, since the trinitrophenyl group seems to be the limit of direct nitration of the phenyl group, it may be predicted that by the direct nitration of the picrylnitranilines higher nitro-members would be formed, and that the nitro-groups would enter into the mononitrophenyl group. If, then, by the nitration of the picrylnitranilines, higher isomeric nitro-compounds were obtained, the isomerism must reside in the nitrated mononitrophenyl group, since the trinitrophenyl group remains unchanged during the nitration. It is, however, very possible that in one of the resulting compounds the two picryl groups may be identical.

Since the positions of the nitro-groups in these dipicrylamines has not been ascertained, the trinitrophenyl group of picric acid will be represented as α, and the dinitromononitrophenyl groups of meta- and paranitraniline as β and γ respectively. Only two of these picryl groups can be identical.

α-Picryl-β-picrylamine.—$C_{12}H_5N_7O_{12} = NH[C_6H_2(NO_2)_3]_2$.—The α-picryl-metanitraniline was added in small portions to a cooled mixture of equal volumes of fuming nitric and concentrated sulphuric acid. The liquid became hot, and a violent reaction set in. After the reaction had subsided the liquid was poured into cold water, whereupon a bright sulphur-yellow cream was obtained. After washing out the acid with water, the cream was well washed with alcohol, which removed a resin, then dissolved in boiling glacial acetic acid, and precipitated by strong hydrochloric acid, the precipitate washed with the dilute acid, and dissolved in boiling glacial acetic acid, with addition of animal charcoal, the solution filtered, and left to crystallise.

The substance is an impalpable sulphur-yellow powder; by careful crystallisation from glacial acetic acid it is obtained in small transparent glittering crystals, melting at 261°, to a red liquid, which solidifies at 175—170° to a red glass. On touching it with a hard body when in the liquid state, it solidifies to a yellow amorphous mass.

It is almost insoluble in hot water, and in dilute hydrochloric, nitric, and sulphuric acids. In hot amyl and ethyl alcohols it is almost insoluble, hardly soluble in ether, carbon tetrachloride, chloroform, and carbon disulphide; difficultly soluble in cold glacial acetic acid, easily on boiling; easily soluble in aniline. In aqueous ammonia, soda, and potash it dissolves easily, with a splendid scarlet colour; when boiled with the fixed alkalis it gives off ammonia. In sodium carbonate it dissolves easily, forming the sodium salt.

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* Willgerodt announced (*Deut. Chem. Ges. Ber.*, ix, 1178), a dinitrophenylmetanitraniline which he had produced by the action of α-$C_6H_3(NO_2)_2Cl$ on metanitraniline. M. p. 194·5°. Perhaps identical with the above.

By addition of water to the solution in boiling glacial acetic acid, a thick precipitate is formed, which after crystallisation from glacial acetic acid has a melting point of 205°, and on analysis proved to be the original picrylmetanitraniline, from which this dipicrylamine was prepared. *By the addition, then, of water to the boiling solution in glacial acetic acid, the α-β-picrylamine loses two nitro-groups, and is reconverted into the picrylmetanitraniline.*

The dipicrylamine does not explode by percussion. When heated, it puffs with a white luminous flame, and leaves a light porous coal. It explodes with violence when thrown on to hot platinum foil.

α-Picryl-γ-picrylamine, $C_{12}H_5N_7O_{12} = NH[C_6H_2(NO_2)_3]_2$.—This compound was prepared by nitration of picrylparanitraniline in the same manner as in the case of the preceding compound. On pouring the resulting mixture into cold water, the substance separated as a light greenish-yellow cream, which was extracted with alcohol and crystallised from glacial acetic acid. It then forms small, transparent, glittering, light-yellow prisms, with a green reflex. It fuses at 230°, with decomposition. Its solubility is about the same as that of the preceding compound. It puffs on being heated, and explodes with violence when thrown on a hot surface. With alkalis it behaves like the α-β-compound.

It has already been mentioned that these compounds, especially the dipicrylamines, give fine scarlet colours with alkalis. The author finds that these colours are caused by the formation of salts of the nitrodiphenylamines. The hydrogen-atom of the imido-group becomes so strongly negative by the introduction of the nitro-groups, that it can easily be replaced by basic atoms.

Of the numerous salts prepared, one only has been examined, viz., *Barium α-picryl-β-picryldiamine*, $C_{24}H_8N_{14}O_{24}Ba$

$$= \left.\begin{matrix}\alpha\text{-}C_6H_2(NO_2)_3\\ \beta\text{-}C_6H_2(NO_2)_3\end{matrix}\right\} N{-}Ba{-}N \left\{\begin{matrix}C_6H_2(NO_2)_3\ \alpha\\ C_6H_2(NO_2)_3\ \beta\end{matrix}\right. \cdot$$

The α-β-picrylamine was added to a cream of barium hydrate; it dissolved immediately with a deep red colour. The solution was boiled for a few minutes, and then evaporated to the crystallising point. On cooling, dark red needles were formed, which were purified by recrystallisation from water.

This compound appears to have sufficient basic properties to form salts with weak acids. Thrown on a hot surface it explodes violently.

Ammonium-α-γ-picrylamine crystallises in fine deep red transparent rhombohedrons.(?) It is possibly identical with the dye-stuff "aurantia." By treatment of the sodium salts of the dipicrylamines with picryl chloride, a reaction takes place, doubtless with the formation of the tertiary picrylamine, $N[C_6H_2(NO_2)_3]_3$.

The following table will show the various nitrodiphenylamines known, their mode of preparation, and their properties.

No.	Rational formula.	Empirical formula.	Remarks.
I	$N\left\{\begin{matrix}C_6H_5\\C_6H_4(NO_2)\\CO.C_6H_5\end{matrix}\right.$	$C_{19}H_{14}N_2O_3$	By the action of HNO_3 on $N\left\{\begin{matrix}(C_6H_5)_2\\CO.C_6H_5\end{matrix}\right.$. Light-yellow crystals.
II	$N\left\{\begin{matrix}C_6H_5\\C_6H_4(NO_2)\\H\end{matrix}\right.$	$C_{12}H_{10}N_2O_2$	NaHO on No. I.
III	$N\left\{\begin{matrix}C_6H_4(NO_2)\\C_6H_4(NO_2)\\CO.C_6H_5\end{matrix}\right.$	$C_{19}H_{13}N_3O_5$	Fuming HNO_3 on $N\left\{\begin{matrix}(C_6H_5)_2\\CO.C_6H_5\end{matrix}\right.$. Deep-yellow crystalline substance.
IV	$N\left\{\begin{matrix}C_6H_4(NO_2)\\C_6H_4(NO_2)\\H\end{matrix}\right.$	$C_{12}H_9N_3O_4$,	NaOH on No. 3. Reddish-yellow needles with metallic blue reflex.
V	$N\left\{\begin{matrix}C_6H_5\\C_6H_3(NO_2)_2{}^{m.}\\H\end{matrix}\right.$	$C_{12}H_9N_3O_4$.	$C_6H_3(NO_2)_2Br$ on $C_6H_5NH_2$. Long thin scarlet or red-yellow needles, m.-p. 153° (Clemm). a-$C_6H_3(NO_2)_2Cl$ on alcoholic H_2S solution of aniline, m.-p. 156—157° (Willgerodt).
VI	$N\left\{\begin{matrix}C_6H_5\\C_6H_2(NO_2)_3{}^{a}\\H\end{matrix}\right.$	$C_{12}H_8N_4O_6$	$C_6H_2(NO_2)_3Cl$ on $C_6H_5NH_2$. Sparkling prisms. Scarlet by reflexion; reddish-yellow by refraction. M.-p. 175°.
VII	$N\left\{\begin{matrix}C_6H_4(NO_2)^{m}\\C_6H_3(NO_2)_2{}^{m}\\H\end{matrix}\right.$	$C_{12}H_8N_4O_6$	$C_6H_3(NO_2)_2Br$ on m-nitraniline. Small glittering yellow crystals. M.-p. 189°.
VIII ...	$N\left\{\begin{matrix}C_6H_4(NO_2)^{p}\\C_6H_3(NO_2)_2{}^{m}\\H\end{matrix}\right.$	$C_{12}H_8N_4O_6$	$C_6H_3(NO_2)_2Br$ on p-nitraniline. Light electrical yellow powder. Easily soluble in cold glacial acetic acid. M.-p. 181°.
IX	$N\left\{\begin{matrix}C_6H_4(NO_2)^{m}\\C_6H_2(NO_2)_3a\\H\end{matrix}\right.$	$C_{12}H_7N_5O_8$	$C_6H_2(NO_2)_3Cl$ on m-nitraniline. Heavy cryst. yellow sand or wine-yellow transparent prisms. M.-p. 205°.

No.	Rational formula.	Empirical formula.	Remarks.
X......	$N\left\{\begin{matrix}C_6H_4(NO_2)p\\C_6H_2(NO_2)_3\alpha\\H\end{matrix}\right.$	$C_{12}H_7N_5O_8$	$C_6H_2(NO_2)_3Cl$ on *p*-nitraniline. Red crystalline powder or crystalline scales. M.-p. 216°.
XI	$N\left\{\begin{matrix}C_6H_2(NO_2)_3\beta\\C_6H_2(NO_2)_3\alpha\\H\end{matrix}\right.$	$C_{12}H_5N_7O_{12}$	By nitration of IX, m.-p. 261°. Impalpable bright yellow powder or small transparent glittering yellow crystals.
XII....	$N\left\{\begin{matrix}C_6H_2(NO_2)_3\gamma\\C_6H_2(NO_2)_3\alpha\\H\end{matrix}\right.$	$C_{12}H_5N_7O_{12}$	By nitration of X. Small transparent glittering bright-yellow prisms with a green reflex. M.-p. 230°.
XIII...	$Ba\left\{\begin{matrix}N\left\{\begin{matrix}C_6H_2(NO_2)_3\beta\\C_6H_2(NO_2)_3\alpha\end{matrix}\right.\\N\left\{\begin{matrix}C_6H_2(NO_2)_3\beta\\C_6H_2(NO_2)_3\alpha\end{matrix}\right.\end{matrix}\right.$	$C_{24}H_8N_{14}O_{24}Ba$	$Ba(OH)_2$ on XI. Dark saffron-red glittering needles. Explodes on heating.
XIV ...	$N\left\{\begin{matrix}C_6H_2(NO_2)_3\,?\\C_6H_2(NO_2)_3\,?\\H\end{matrix}\right.$	$C_{12}H_5N_7O_{12}$	Nitration of diphenylamine. Transparent light-yellow prisms. M.-p. 238°.
XV	$N\left\{\begin{matrix}C_6H_2(NO_2)_3\,?\\C_6H_2(NO_2)_3\,?\\NH_4\end{matrix}\right.$	$C_{12}H_8N_8O_{12}$	NH_3 on XIV. Beautiful red leaves.
XVI ...	$N\left\{\begin{matrix}C_6H_2Br(NO_2)_2\,?\\C_6H_2Br(NO_2)_2\,?\\H\end{matrix}\right.$	$C_{12}H_5N_5BrO_8$	Nitration of— $HN\left\{\begin{matrix}C_6H_4Br\\C_6H_3Br_2\end{matrix}\right.$. Yellow pearly leaves or rhombic tablets. M.-p. 235—240—242°.
XVII ..	$N\left\{\begin{matrix}C_6H_2(NO_2)_2Br\\C_6H_5\\H\end{matrix}\right.$	$C_{12}H_8N_3BrO_4$	$C_6H_5NH_2$ on— $C_6H_2\left\{\begin{matrix}(NO_2)_2\beta\\Br_2p\end{matrix}\right.$. Beautiful red-orange fine hairy needles. M.-p. 120.°
XVIII..	$N\left\{\begin{matrix}C_6H_2(NO_2)_2Br\,?\\C_6H_3(NO_2)_2\\H\end{matrix}\right.$	$C_{12}H_5N_5BrO_8$	Nitration of XVII. Small brown scales. M.-p. 167·5°.

No.	Rational formula.	Empirical formula.	Remarks.
XIX ...	$N\left\{\begin{array}{l}C_6H_3(NO_2)_2?\\C_6H_4.C_6H_4.NH_2?\\H\end{array}\right.$	$C_{18}H_4N_4O_4$	α-$C_6H_3(NO_2)_2Cl$ on benzidine. Short bluish brown-red needles. M.-p. 255°.
XX	$N\left\{\begin{array}{l}C_6H_3(NO_2)_2?\\C_6H_4.C_6H_4.NH.C_6H_3(NO_2)_2\\H\end{array}\right.$	$C_{24}H_{16}N_6O_8$	Formed from XIX. Yellow pulverulent powder. Sol. in conc. H_2SO_4 with violet colour. M.-p. 330°.
XXI ...	$N\left\{\begin{array}{l}C_6H_3(NO_2)Cl^m\\C_6H_5\\H\end{array}\right.$	$C_{12}H_9N_2ClO_2$	Action of—$C_6H_3(NO_2)Cl^m(NO_2)$ on aniline. Long glittering alizarin-red needles. M.-p. 108·5°.

C. W. W.

Base derived from a Waste-product in the Aniline Manufacture. By C. LORING JACKSON (*Amer. Jour. Sci.*, xiii, 449).—This body is found in the distillate from the highest boiling fractions of the aniline-distillation and passes over after the toluidine.

The substance, a black oily liquid, was dissolved in hydrochloric acid and filtered from tarry matters; the oily base set free by sodium hydrate was fractioned, and yielded at first xylidine and allied bodies; afterwards a fraction from 280—320°, which, after removal of naphthylamine with dilute sulphuric acid, was converted into the nitrate and purified by crystallisation; it then formed radiate groups of white needles which gave on analysis the composition $C_{13}H_{14}N.NO_3$.

The *sulphate* is very soluble. The *chloride*, $C_{13}H_{14}NCl$, crystallised in flat white needles. The *platinum salt*, $(C_{13}H_{14}NCl)_2PtCl_4$, crystallises in very characteristic fan-like groups of sparingly soluble light-yellow needles.

The free base, $C_{13}H_{13}N$, was obtained as an oil, which gave with chloroform and potassium hydrate a smell similar to that of the isocyanides; it is therefore a primary amine, $C_{13}H_{11}NH_2$. An acetyl-compound, $C_{13}H_{11}.NH.C_2H_3O$, was prepared and crystallised in white needles melting at 114·25°.

This base differs from the one which Carnelley prepared (this *Journal*, 1876, i, 21) by the reduction of synthetically formed mononitrotolylphenyl, in the following properties. Carnelley found that on adding sodium hydrate to a salt of his base, extracting with ether, and evaporating the ether, an oily body was first produced, from which there separated out a small quantity of needle-shaped tufts melting at 93—97°. The crystals obtained by treating a salt of the present base in a similar manner melted at 46—70°, and were moderately large prismatic crystals arranged in pennate groups, breaking up on pressure into rough octohedral masses. The crystals were insoluble in water, freely soluble in alcohol, ether, and benzene, and instantly converted by hydrochloric acid into a chloride easily soluble in water, and separating therefrom in white flattened needles melting with decomposition at about 200°; whereas Carnelley's crystalline base, when heated with hydrochloric acid, dissolved only after long boiling, and separated from the solution in small needles, melting with decomposition at 280—283°.

From this comparison it is evident that the two bases are not identical but isomeric. C. W. W.

Metamorphoses of Aniline-Black. By F. GOPPELSRÖDER (*Dingl. polyt. J.*, ccxxiv, 439—448).—1. *On Aniline-black vat.* The basis of electrolytic aniline-black obtained by treating the black formed at the positive pole, after purification with boiling water and alcohol, with solution of potash or soda dissolves in fuming sulphuric acid, and, according to the quantity of acid used, the solution has a bluish-violet or dark-green colour. If the action of the fuming acid has taken place in a satisfactory manner, a green precipitate should be produced by adding water to the solution, while the latter should be colourless or coloured slightly reddish-violet. After washing the precipitate until it no longer shows an acid reaction, it is dissolved by continuing the washing with water, the solution formed having a green colour. Cotton (mordanted or not mordanted) is not dyed by this solution, but wool is turned blue on the addition of ammonia. Caustic potash or soda changes the green solution to blue, and, after warming, to violet; acids bring the blue back to its original colour. The green solution is rendered colourless by hydrogen sulphide or by zinc-powder. The colourless liquid assumes a green colour on addition of fuming nitric acid. The following table gives various other reactions of the green solution:—

Green Solution.		Green Solution from Green Precipitate.	
Reagents.	Change.	Reagents.	Change.
Sodium amalgam.	Bluish-violet; then slowly discoloured.	Sulphuretted hydrogen	Green.
Ferrous sulphate.	No reduction.	Chlorine-water..	Violet.
Sulphuric acid . Thiosulphate of sodium	No reaction.	Acetate of lead..	Green precipitate.
Hyposulphite of zinc or calcium.	Yellow colour.	Tetrachloride or dichloride of tin	Green precipitate.
Hypochlorite of sodium	Red when cold; orange-red on warming. Addition of SO_2, yellow.	Bichromate of potassium	Black precipitate.
Bichromate of potassium	Green.	Hypochlorite of potassium	Bluish-violet, then reddish-violet colour; SO_2, green
		Excess of the former	Reddish-yellow; SO_2, no change; $Na_2S_2O_3$, brown colour.

Green Solution.		Green Solution from Green Precipitate.	
Reagents.	Change.	Reagents.	Change.
Permanganate of potassium	Discoloured after adding sulphuric acid.	Sulphuretted hydrogen	The above bluish-violet or reddish-violet solution turns yellow.
Chlorine-water...	Intensely green, then bluish-violet, finally wine-red; NH_3, yellow.	Hypochlorite of sodium	Orange-yellow,
Ferricyanide of potassium and sodium	Brown.	Sodium amalgam	Yellowish-brown, and violet by adding hypochlorite of sodium.
Sulphate of copper	Green precipitate.		
Baryta-water	Green precipitate.		

If the sulphuric acid used for treating the basis of aniline-black is not sufficiently concentrated, a green precipitate is produced which is insoluble in water. Neither of these green precipitates can be converted into aniline-black by ozone or other well-known reagents. The green precipitate or its green aqueous solution, when neutralised with alkalis, gives a blue liquid with violet tinge exhibiting the following reactions:—

Blue Alkaline Solution.

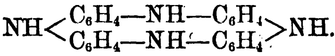
Reagents.	Change of Colour.
Hydrochloric acid	Green.
Hypochlorite of sodium.......	Reddish-violet when cold; orange-red when warm. Excess gives a yellow colour.
Ferricyanide of potassium.....	Yellowish-brown; acetic acid, hydrochloric acid, &c. Green.
Bromine	Bluish-violet. Excess destroys the colour.
Chlorine water...............	The same.
Fuming nitric acid	Green; then destroyed.
Glucose.....................	Reduces the blue solution.

On introducing vegetable or animal fibres into a concentrated vat of aniline-black, they assume a violet colour, then a bluish-violet, and, finally, a blue colour, which is turned green by dilute acids, and not altered by alcohol. Alkalis, however, dissolve the blue colour with violet tinge. By treating the blue fibres in an oxidising bath a black is obtained which is not turned green by acids. If the blue was light, a grey colour is obtained; if it was dark, a black is formed. Calcium hyposulphite or metallic zinc reduces the alkaline bluish-violet solution in the same manner as glucose. The liquid assumes a yellow colour, while cotton dipped into it is dyed blue. The author has not yet succeeded in obtaining a black vat similar to the indigo vat with iron-vitriol and lime. He obtained a black deposit (coated with a bluish-violet precipitate) from a black lake containing lime and iron, as shown by the decomposition with hydrochloric acid, while the black was thrown down without any change. The following method gives a dark black colour in the vat:—The cloth is treated in the vat several times, and exposed to the air each time till a very dark blue colour has been obtained, which is then oxidised according to Jeanmaire's process with an acidulated solution of ferric chloride; this operation is repeated until the desired black shade is obtained. The reduced aniline-black may be used as ink; the letters are at first but slightly coloured, but afterwards assume a blue and, finally, a dark black colour. For instance, by painting on paper with the black vat containing an excess of glucose, we obtain shades varying according to the number of coats, from a light grey to a dark black colour. Sulphuretted hydrogen changes the black to brownish-yellow, which is blackened on oxidation in the air. Hypochlorite of calcium gives a reddish-violet colour; and afterwards destroys it; acids give a green colour, which ammonia turns black, and alkalis give a violet colour.

The above-described reduction by glucose in presence of alkali takes place also with the derivative of the basis of commercial aniline-black in the same way as with the basis of the electrolytic black. The commercial substance, however, requires purification with hot water and alcohol.

With regard to an illustration of the above facts and a theory as to the relation of aniline-black to various bodies connected therewith, the author can at present give only a provisional explanation. For the basis of electrolytic aniline-black he obtained the formula $C_{24}H_{20}N_4$. His analyses rested between the following two rational formulæ:—

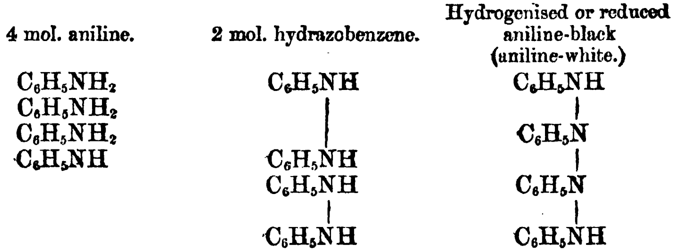
$$(C_6H_5)N—(C_6H_5)N—(C_6H_5)N—(C_6H_5)N \text{ and}$$



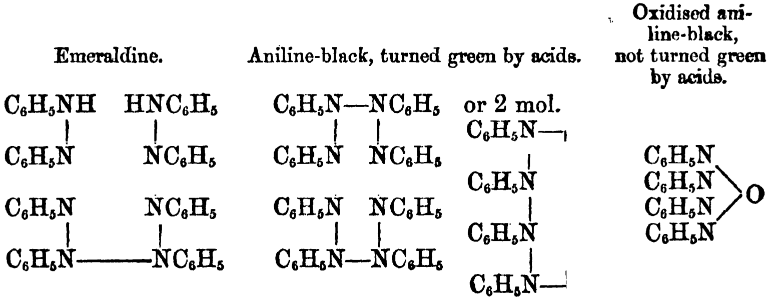
$$NH\begin{matrix}< \\ \ \end{matrix}\!\!\begin{array}{l} C_6H_4—NH—C_6H_4 \\ C_6H_4—NH—C_6H_4 \end{array}\!\!\begin{matrix}> \\ \ \end{matrix}NH.$$

The above facts are best explained by assuming the first formula as correct. The basis of aniline-black, a tetrazo-compound, is converted into the sulpho-acid by means of fuming sulphuric acid, which gives a colourless hydrogenised derivative, and with alkalis salts which dissolve in water, forming bluish-violet solutions. These are rendered colourless by hydrogenising agents, but become blue by dehydrogenation in the air, and give a black, which by superoxidation is converted into the above-named substance, not turned green by acids. As oxidising agents, aqueous solutions of potassium chlorate with addition of cupric sulphate and sal-ammoniac, or potassium chlorate with cupric chloride, or potassium bichromate, or, better, the well-known Jeanmaire agent, were employed. In the development of aniline-black in acid solutions of the aniline salts, the product first formed is emeraldine, a green body which should not be regarded as identical with that which is obtained by pouring the solution of aniline-black in fuming sulphuric acid into water.

The following bodies, therefore, have to be accurately investigated by analysis and metamorphoses :—(1.) Emeraldine, the mean between fugitive black and the aniline salts. (2.) The black which is turned green by acids. (3.) The oxidised true black. (4.) The green product of the action of fuming sulphuric acid on the black which turns green and on the real black. (5.) The colourless product of the hydrogenation of this green body (4) which may at present be called the sulpho-acid of the reduced aniline-black, or aniline-white. Taking the aniline salts as a starting-point, these various bodies are produced in the following order:—Aniline salts, emeraldine, black, sulpho-acid of the black, sulpho-acid of the hydrogenised black, and, by oxidation, once more the black. The following, at present purely hypothetical formulæ, may serve to explain the formation of aniline-black from the aniline salts, and the relation of the various bodies at present observed by the author:—


4 mol. aniline. 2 mol. hydrazobenzene. Hydrogenised or reduced aniline-black (aniline-white.)

$$\begin{array}{ccc}
\begin{array}{c} C_6H_5NH_2 \\ C_6H_5NH_2 \\ C_6H_5NH_2 \\ C_6H_5NH \end{array} &
\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5NH \\ C_6H_5NH \\ | \\ C_6H_5NH \end{array} &
\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5N \\ | \\ C_6H_5N \\ | \\ C_6H_5NH \end{array}
\end{array}$$


Emeraldine. Aniline-black, turned green by acids. Oxidised aniline-black, not turned green by acids.

$$\begin{array}{ccc}
\begin{array}{cc} C_6H_5NH & HNC_6H_5 \\ | & | \\ C_6H_5N & NC_6H_5 \\ C_6H_5N & NC_6H_5 \\ | & | \\ C_6H_5N & \text{———} NC_6H_5 \end{array} &
\begin{array}{cc} C_6H_5N\text{—}NC_6H_5 \\ |\quad\ | \\ C_6H_5N\ \ NC_6H_5 \\ C_6H_5N\ \ NC_6H_5 \\ |\quad\ | \\ C_6H_5N\text{—}NC_6H_5 \end{array}
\text{ or 2 mol. }
\begin{array}{c} C_6H_5N\text{—} \\ | \\ C_6H_5N \\ | \\ C_6H_5N \\ | \\ C_6H_5N\text{—} \end{array} &
\begin{array}{c} C_6H_5N \\ C_6H_5N \\ C_6H_5N \\ C_6H_5N \end{array} \!\!\! > O
\end{array}$$

2. *Conversion of the Base of Aniline-black into a Pink fluorescent Colouring Matter.*—The basis of the electrolytic aniline-black was fused with potassium bisulphate. Sulphurous acid and nitrogen were given off, and the fused mass contained neither sulphite, thiosulphate, nor sulphide, and gave when boiled with water a slight yellow colour. The residue insoluble in water was treated on the water-bath with concentrated sulphuric acid, and yielded a copious black precipitate on the addition of water. The reddish-violet solution was rendered fluorescent by ammonia. The precipitate was treated with alcohol, which extracted a pink colouring matter showing the same fluorescence and giving the same chemical reactions and spectrum analysis as naphthalene-pink. The change of the black into the pink colouring matter is regarded by the author as an act of dehydrogenation. Should this

body prove to be naphthalene-pink, its formation would be explained by the following equation:—

$$5C_{24}H_{20}N_4 - 16H - 8N = 4C_{30}H_{21}N_3.$$

The reaction between the black and the bisulphate would be:

$$5C_{24}H_{20}N_4 + 16HKSO_4 = 8N + 16H_2O + 8SO_2 + 8K_2SO_4 + 4C_{30}H_{21}N_3.$$

The bisulphate is decomposed in the following manner:—

$$2KHSO_4 = K_2SO_4 + H_2O + O + SO_2.$$

In conclusion it is mentioned that on treating the basis of aniline-black with bichromate of potassium, and boiling it with water and then with alcohol acidified with sulphuric acid, the latter assumes a light violet colour. On treating the residue with caustic potash it assumes a violet-pink colour, while the residue when treated with alcohol gives a blue colouring matter. The same result was obtained with the basis of the aniline-black prepared in the usual way; but with the salt, *i.e.*, the deposit, as formed on the positive pole or with the commercial salt, different results were obtained. D. B.

Amidazo-compounds in the Tolyl Series. By R. Nietzki (*Deut. Chem. Ges. Ber.*, x, 1155—1160).—The metatoluidine employed was prepared by Beilstein and Kuhlberg's method from metanitro-paratoluidine, the yield being about 10 per cent. of the paratoluidine. When treated with nitrous acid, either in alcoholic solution or floating on a solution of salt, it is easily converted into meta-amidazo-toluene, the hydrochloride of which is much less soluble than that of the corresponding ortho-compound previously described. The hydrochloride forms dark steel-blue needles, which are only slightly soluble in boiling alcohol, and are decomposed by water. The base itself crystallises in golden-yellow needles, which melt at 80°. The platinum salt, $(C_{14}H_{15}N_3.HCl)_2PtCl_4$, forms thin plates almost insoluble in water and in alcohol. On mixing alcoholic solutions of metatoluidine and paradiazoamidotoluene, paratoluidine is liberated, and metadiazoamidotoluene is formed. This base crystallises from alcohol in large yellow plates which melt at 127°. The hydrochloride forms small steel-blue plates grouped in stars; and the platinum salt, $(C_{14}H_{15}N_3.HCl)PtCl_4$, small bronze needles difficultly soluble.

It was important to ascertain what the reduction-products of the amidazo-compounds were, as if the amido- and azo- groups were 1 : 4, the resulting diamidotoluenes should yield toluquinone on oxidation.

In a former communication the author noticed that the action of oxidizing agents on paradiamidotoluene gave a beautiful green colour, but he now finds that when perfectly pure it no longer gives the colour reaction, although toluquinone melting at 67° is readily obtained. The hydroquinone melts at 124°. Pure paradiamidotoluene, obtained from the acetyl-derivative by heating it at 150° with hydrochloric acid, crystallises from hot dilute alcohol in large colourless prisms, which melt at 64° and boil at 273—274°. The green colour reaction is due to the presence of a trace of orthotoluidine, and as the same effect is produced with orthotoluidine and the base obtained by the reduction of meta-amidoazotoluene, he considers there can be no doubt as to its being the same diamidotoluene. These facts tend to strengthen the opinion that the quinones are 1 : 4 or para-compounds, and it would also seem that in all the amido-azo compounds the amido- and azo-groups occupy the positions 1 : 4 respectively.

C. E. G.

Paradibromobenzenesulphonic Acid and some Derivatives. By H. BORNS (*Liebig's Annalen*, clxxxvii, 350—372).—1. *Paradibromobenzenesulphonic acid*, $C_6H_3Br_2SO_3H,3H_2O$.—The author obtains this acid by heating paradibromobenzene (melting at 89°) to 100° with fuming sulphuric acid for several days. On evaporating its aqueous solution over sulphuric acid it crystallises in fine transparent prisms, soluble in water and alcohol, and melting about 98°. It gives off 2 mols. of water at 100°, and the rest at 130°. The anhydrous acid melts at 128°.

The *ammonium salt*, $C_6H_3Br_2SO_3NH_4$, forms delicate needles very easily soluble in water and alcohol.

The *potassium salt*, $C_6H_3Br_2SO_3K,H_2O$, crystallises in long prisms or needles, which dissolve easily in water, and fall to powder when dried.

The *sodium salt*, $C_6H_3Br_2SO_3Na,1\frac{1}{2}H_2O$, forms delicate silky needles.

The *barium salt*, $(C_6H_3Br_2SO_3)_2Ba,H_2O$, forms pearly laminæ, which lose their water at 140° only.

The *calcium salt*, $(C_6H_3Br_2SO_3)_2Ca,10H_2O$, crystallises from concentrated solutions in pointed needles, and from weaker solutions in laminæ, easily soluble in water and alcohol. The crystals effloresce rapidly in the air.

The *lead salt*, $(C_6H_3Br_2SO_3)_2Pb,3H_2O$, forms yellowish laminæ, which dissolve sparingly in water, but are gradually deposited from the solution on standing.

The *silver salt*, $C_6H_3Br_2SO_3Ag,5H_2O$, crystallises in white prisms or in long pointed needles, which when dry do not alter in the air.

The *chloride*, $C_6H_3Br_2SO_2Cl$, is easily obtained by treating the potassium salt with phosphorus pentachloride. It crystallises from ether in tables, or in pearly laminæ, which melt at 71—72°.

The *amide*, $C_6H_3Br_2SO_2NH_2$, formed by the action of strong ammonia on the chloride, crystallises in long needles which dissolve sparingly in cold water and melt at 193°.

2. *Nitroparadibromobenzenesulphonic acid*, $C_6H_2Br_2(NO_2)SO_3H,1\frac{1}{2}H_2O$.—This substance is obtained by boiling the foregoing acid with the strongest nitric acid in a retort. It crystallises from aqueous solution over sulphuric acid in small yellow hygroscopic prisms, which dissolve in alcohol and ether, and blacken at 100° without melting.

The *ammonium salt*, $C_6H_2Br_2(NO_2)SO_3NH_4,\frac{1}{2}H_2O$, forms small laminæ, which dissolve easily in water, alcohol, and ether, give off their water completely at 130°, and decompose at 150°.

The *potassium salt*, $C_6H_2Br_2(NO_2)SO_3K,H_2O$, crystallises in fine yellow needles, easily soluble in water and alcohol.

The *barium salt*, $[C_6H_2Br_2(NO_2)SO_3]_2Ba,1\frac{1}{2}H_2O$, forms yellow prisms, easily soluble in hot, sparingly in cold water. This salt crystallises also with 6 mol. and with 9 mol. of water.

The *calcium salt*, $[C_6H_2Br_2(NO_2)SO_3]_2Ca,3H_2O$, forms small yellow prisms, easily soluble in water and alcohol.

The *lead salt*, $[C_6H_2Br_2(NO_2)SO_3]_2Pb,3H_2O$, crystallises in yellow nodules, easily soluble in water and alcohol.

The *chloride*, $C_6H_2Br_2(NO_2)SO_2Cl$; is most easily obtained by heating the potassium salt to 120° with phosphorus pentachloride and oxychloride in a sealed tube. It dissolves freely in ether, and crystallises imperfectly on evaporating the solution.

The *amide*, $C_6H_2Br_2(NO_2)SO_2NH_2$, is formed with difficulty by warming the chloride with strong ammonia, or better, by heating the two substances to 100° in sealed tubes. When crystallised repeatedly from hot water and alcohol it forms greenish-yellow prisms, which dissolve easily in hot water and alcohol, and melt at 178°.

3. *Amidoparadibromobenzenesulphonic acid*, $C_6H_2Br_2(NH_2)SO_3H,\frac{1}{2}H_2O$.—Formed, together with other products, by the action of tin and hydrochloric acid on nitrodibromobenzenesulphonic acid. It crystallises from strong solutions in delicate white needles and from weak solutions in faint violet-coloured prisms, which decompose at 150° without melting. It is sparingly soluble in hot and cold water and in alcohol. The salts are all easily soluble.

The *potassium salt*, $C_6H_2Br_2(NH_2)SO_3K$, crystallises in fine monoclinic tables.

The *barium salt*, $[C_6H_2Br_2(NH_2)SO_3]_2Ba,H_2O$, forms transparent prisms, which turn red in the air. It dissolves easily in alcohol.

The *lead salt*, $[C_6H_2Br_2(NH_2)SO_3]_2Pb,8H_2O$, crystallises in small white needles or pale brown prisms.

4. *Tribromobenzenesulphonic acid*, $C_6H_3Br_3SO_3H$.—The author obtains this substance by passing nitrous acid into a solution of amidodibromobenzenesulphonic acid in weak spirit, and evaporating the diazo-compound thus formed with strong hydrobromic acid. The residue is converted into barium salt, which is purified by repeated crystallisation. The free acid has not been examined.

The *sodium salt*, $C_6H_2Br_3SO_3K,1\frac{1}{2}H_2O$, forms brilliant yellow prisms, freely soluble in hot water.

The *barium salt*, $(C_6H_2Br_3SO_3)_2Ba,2H_2O$, forms yellow prisms, which dissolve with great difficulty in water.

The *chloride*, $C_6H_2Br_3SO_2Cl$, and the *amide*, $C_6H_2Br_3SO_2NH_2$, have also been prepared. The latter crystallises in small needles, which dissolve easily in alcohol, and undergo decomposition above 200°.

5. *Paradibromobenzenedisulphonic acid*, $C_6H_2Br_2(SO_3H)_2$, is formed, together with the corresponding monosulphonic acid, by the action of fuming sulphuric acid on dibromobenzene. It crystallises in small, transparent, easily soluble prisms.

The *potassium salt*, $C_6H_2Br_2(SO_3K)_2$, forms white soluble needles.

The *barium salt*, $C_6H_2Br_2(SO_3)_2Ba,4\frac{1}{2}H_2O$, crystallises in small, white, easily soluble needles.

The *chloride*, $C_6H_2Br_2(SO_2Cl)_2$, forms transparent monoclinic crystals, melting at 161°.

The *amide*, $C_6H_2Br_2(SO_2NH_2)_2$, forms nodules of microscopic needles, easily soluble in water and alcohol.

Dibromobenzenedisulphonic acid is converted by boiling with strong nitric acid into *nitrodibromobenzenedisulphonic acid*, which is easily reduced by tin and hydrochloric acid to the corresponding *amido-acid*, $C_6HBr_2(NH_2)(SO_3H)_2$. The latter forms small crystals easily soluble in water and alcohol; its potassium and barium salts are crystalline and easily soluble. The *chloride* crystallises in prisms melting at 148°. The *amide* forms small needles which melt at 206°.

6. *Amidobromobenzenesulphonic acid*, $C_6H_3Br(NH_2)SO_3H$ + aq., obtained by the action of fuming sulphuric acid on parabromacetanilide at 170—180°, crystallises in white silky needles or in large pale-brown prisms, which dissolve sparingly in water and alcohol.

The *ammonium salt*, $C_6H_3Br(NH_2)SO_3NH_4$, forms small, reddish, easily soluble needles.

The *potassium salt*, $C_6H_3Br(NH_2)SO_3K$, crystallises in transparent laminæ or prisms, easily soluble in water.

The *barium salt*, $[C_6H_3Br(NH_2)SO_3]_2Ba,HO_2$, forms pearly laminæ, which turn red while moist, and dissolve easily in water and weak spirit.

The *calcium salt*, $[C_6H_3Br(NH_2)SO_3]_2Ca,H_2O$, forms easily soluble small prisms.

Amidobromobenzenesulphonic acid suspended in a little strong alcohol and treated with nitrous acid, yields the *diazo-compound*, $C_6H_2BrN_2SO_3H$, which crystallises in small yellow prisms, turning red in the light. This compound, when heated with hydrobromic acid, yields paradibromobenzenesulphonic acid, identical with that formed by the action of sulphuric acid on paradibromobenzene. When heated with absolute alcohol it yields metabromobenzenesulphonic acid.

J. R.

Iodobenzenesulphonic Acid. By W. LENZ (*Deut. Chem. Ges. Ber.*, x, 1135—1137).—Körner and Paternò obtained paraiodobenzenesulphonic acid by the action of sulphuric acid on benzene. The author, however, prepared it by the action of hydriodic acid on the diazo-compound from sulphanilic acid. After removal of iodine and excess of hydriodic acid, it was converted into the barium salt, crystallised, and then exactly decomposed with sulphuric acid. It crystallises in needles, which are very soluble in water, alcohol, and ether. $Ca(C_6H_4ISO_3)_2$, $Ba(C_6H_4ISO_3)_2$, and $Pb(C_6H_4ISO_3)_2$, all form colourless microscopic crystals, the first being easily soluble, and the last two difficultly soluble in water. The potassium and ammonium salts crystallise in minute needles. The chloride, $C_6H_4I.SO_2Cl$, crystallises in large transparent prisms, which melt at 86—87°, whilst the amide, $C_6H_4ISO_2.NH_2$, forms microscopic plates melting at 183°. The author has also obtained a fluobenzenesulphonic acid by a similar process, but all its compounds are so soluble that they could not be purified, except the amide, $C_6H_4F.SO_2NH_2$. This forms colourless, microscopic, six-sided, rhombic plates, easily soluble in alcohol. Potassium cyanide also acts strongly on the diazo-compound of sulphanilic acid, but the author has not yet investigated the nature of the reaction.

C. E. G.

Derivatives of Metabenzene-disulphonic Acid. By G. HEINZELMANN (*Liebig's Annalen*, clxxxviii, 157—184).—The best way of preparing this acid is to heat benzene with its own volume of fuming sulphuric acid, and then to add to this solution an equal volume of the same acid, and heat the mixture in a retort with its neck directed upwards, for two or three hours to such a degree that whilst the retort is well filled with white vapours, little or none shall escape; if only one hour's heating be allowed, much benzenemonosulphonic acid is found in the product. The thick dark-coloured mass is dissolved in water and the solution is neutralized with slaked lime; the whole is then drained and freed from colouring matter by treating a portion with sulphuric acid to precipitate the calcium; boiling the filtrate with lead carbonate; adding the resulting lead salt to the remainder; and precipitating the lead with sulphuretted hydrogen. Nearly all colouring matter is thus removed, so that on adding potassium carbonate, a nearly colourless solution of potassium salt is obtained, yielding fine crystals on evaporation. These were recrystallised and converted into the chloride (melting at 63°), which was then decomposed by water at 130—140° after crystallisation from ether:' benzenesulphonic chloride was found in the ethereal mother-liquors.

It was not found practicable to brominate the disulphonic acid, but on nitration it yielded two *nitrobenzenedisulphonic acids*, designated by the author as α and β. The barium salt of the first crystallises in needles, that of the latter in nodules, so that the two can be mechanically separated. The *ammonium salt* of this α-acid, $C_6H_3(NO_2)(SO_3.NH_4)_2$, crystallises anhydrous from the solution obtained by decomposing the barium salt with ammonium carbonate, forming slightly yellow, large flat prisms with sharp end-faces. The *potassium salt* is also anhydrous; it forms colourless fine needles, somewhat less readily soluble in water than the *barium salt*, which crystallises with 4, 5, and $6H_2O$. The *calcium salt*, $C_6H_3(NO_2)\{(SO_3)_2Ca\},2H_2O$, crystallises in slightly yellow, highly deliquescent monoclinic (?) prisms. The *lead salt* forms nearly colourless needles, readily soluble in water, and crystallises with $4H_2O$, whilst the *silver salt* forms anhydrous nodules, quickly blackening in daylight. The *chloride* produced from the potassium salt by heating with phosphorus pentachloride and oxychloride in sealed tubes at 120°, washing the product with water and then with ether, and finally crystallising from warm toluene, forms with the toluene a crystalline compound, $C_6H_3(NO_2)(SO_2Cl)_2.C_7H_8$, which rapidly loses toluene in the air. The pure chloride melts at 96°, and when heated to 140° with water, splits up into hydrochloric acid and nitrobenzenesulphonic acid; concentrated ammonia readily converts it into the diamide, $C_6H_3(NO_2)(SO_2.NH_2)_2$, melting at 242°.

β-Nitrobenzenedisulphonic acid is obtained from the barium salt by means of dilute sulphuric acid, as a syrup, from which very minute hygroscopic crystals form on standing over sulphuric acid for a long

time; its salts are much more soluble than those of the α-acid. The *ammonium salt* is anhydrous; the *potassium salt*, $C_6H_3(NO_2)(SO_3K)_2.\frac{1}{2}H_2O$(?), forms nodules consisting of fine microscopic needles; the *barium salt* crystallises with $5H_2O$, the crystals turning yellow in daylight, without losing water. The *lead salt*, $C_6H_3(NO_2)\{(SO_3)_2Pb\}.4H_2O$, is obtained as a crystalline magma by the spontaneous evaporation of a concentrated solution; weaker solutions effloresce strongly. The *β-chloride* is an oil not solidifying in a freezing mixture; with ammonia, or dry ammonium carbonate, it forms only a brown, insoluble resinous product.

Sulphide of ammonium converts these two nitro-acids into the corresponding amido-acids, crystallising respectively with $3H_2O$ and $2\frac{1}{2}H_2O$, and forming neutral and also acid salts. On treatment with bromine-water, the α-acid forms bromanil, the β-acid tribromaniline. Neutral α-amidobenzenedisulphonates are obtained by decomposing the carbonates of the metals with the free acid not in excess, and the acid salts by adding to the neutral ones another equivalent of acid; the *ammonium salts* are $C_6H_3(NH_2)(SO_3.NH_4)_2.H_2O$ and $C_6H_3(NH_2)(SO_3H)(SO_3.NH_4),xH_2O$, the former crystallising in six-sided prisms, very readily soluble in water and spirit, the latter either in colourless flat anhydrous prisms or in hydrated highly deliquescent needles. The *neutral potassium salt* crystallises with $3H_2O$ and $4H_2O$, the *acid salt* with H_2O; the former is not deliquescent, the latter is difficultly soluble in cold water. The *barium salts* are respectively $C_6H_3(NH_2)\{(SO_3)_2Ba\}.3\frac{1}{2}H_2O$ and $\{C_6H_3(NH_2)(SO_3H)SO_3\}_2Ba.5H_2O$, the former being readily, the latter difficultly soluble in water. The *neutral lead salt* crystallises in slightly coloured six-sided prisms containing $3\frac{1}{2}H_2O$; the *acid salt* contains $6H_2O$; the *neutral silver salt* is anhydrous.

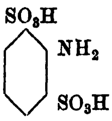
Of the salts of the β-acid the following have been examined: the *neutral barium salt*, $C_6H_3(NH_2)(SO_3)_2Ba.3H_2O$, forms concentric groups of brownish four-sided plates; the acid salt crystallises with $2H_2O$ and separates from hot concentrated aqueous solutions as a bulky mass of slender, shining, microscopic needles, redissolving very slowly in cold water. The *neutral lead salt*, $C_6H_3(NH_2)(SO_3)_2Pb.2H_2O$, forms hard crusts made up of nodules; the acid salt—

$$\{C_6H_3(NH_2)(SO_3H)SO_3\}_2Pb,6H_2O,$$

crystallises in crusts of small, shining, pointed rhombic plates, dissolving very slowly in cold water.

In order to elucidate the structure of these amido-acids, the α-acid was heated with hydriodic acid and phosphorus to 200°, without any result beyond explosion; the results obtained on treatment with bromine, however, point to the α-acid being indicated by No. 3 in the annexed formulæ, whilst the β-acid is indicated either by No. 1 or No. 2, of which the author prefers the latter, as this β-acid appears to be identical with the disulphanilic acid examined by Drebes.

No. 1.



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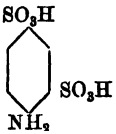

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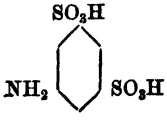

The *diazobenzenedisulphonic acid*, $C_6H_2(SO_3H)_2(N_2)$, obtained on treating the α-amido-acid with nitrous acid does not explode on heating; it decomposes in contact with metallic carbonates, but its acid salts can be obtained by treating the corresponding salts of the amido-acid with nitrous acid; in this way the ammonium salt, $C_6H_2(SO_2H)(SO_3NH_4)(N_2)$, is obtained, crystallising in anhydrous concentrically grouped needles; the potassium salt is anhydrous, whilst the barium salt is—

$$\{C_6H_2(N_2)(SO_3H)(SO_3)\}_2Ba,3H_2O$$

and the lead salt, $\{C_6H_2(N_2)(SO_3H)(SO_3)\}_2Pb,3H_2O$.

Similarly the β-amido-acid forms β-diazobenzenedisulphonic acid, and the acid salts of the β-amido-acid the corresponding β-diazobenzenedisulphonates on treatment with nitrous acid; the potassium salt is anhydrous, the barium salt crystallises with $2H_2O$, and the lead salt with $3H_2O$.

α-Diazobenzenedisulphonic acid boiled with hydrobromic acid forms α-bromodisulphonic acid, $C_6H_3Br(SO_3H)_2$: the ammonium salt of this acid is anhydrous; the potassium salt is very deliquescent and probably contains $4H_2O$; the barium salt crystallises in very soluble needles containing $2\frac{1}{2}H_2O$, and the lead salt in easily soluble, thin prisms containing $2\frac{1}{2}H_2O$. The *chloride*, $C_6H_3Br(SO_2Cl)_2$, crystallises from ether in crusts made up of small nodules melting at 99°; the *amide* melts at 245° and crystallises in white, silky small plates, difficultly soluble in cold, more readily in hot water. The corresponding derivatives of the β-acid have not yet been investigated.

Bromamidobenzenedisulphonic acids.—When 1 mol. bromine is added to an aqueous solution of α-amidobenzenedisulphonic acid, a mixture of mono- and dibromamidobenzenedisulphonic acids is produced, a portion of the amido-acid, however, remaining unchanged; if two or more molecules of bromine be added, bromanil is also formed, and separates in yellow laminæ, its quantity increasing in direct proportion to that of the bromine added. The two bromamido-acids are separated by evaporating the mixed solution to a syrup and leaving it over sulphuric acid for some days; the unaltered amido-acid separates in dense crystals, the mother-liquors of which solidify to a magma of slender needles grouped in nodules. These were converted into barium salt and then into ammonium salt, from the solution of which, prisms and tables separated, consisting of the *ammonium salt of dibromamidobenzenedisulphonic acid;* the last mother-liquors of these deposited the *monobromo-acid* as ammonium salt, crystallising in large, yellowish prisms; the mother-liquors yielded the ammonium salt of amidobenzenedisulphonic acid. The free acids are obtained, by converting the ammonium salts into lead salts, and decomposing with sulphuretted hydrogen, as crystallised masses, mostly consisting of colourless prisms, readily soluble in water and containing respectively $C_6H_2Br(NH_2)(SO_3H)_2.2\frac{1}{2}H_2O$ and $C_6HBr_2NH_2(SO_3H)_2.4H_2O$. *Bromamidobenzenedisulphonate of ammonium* is anhydrous (?); it forms large prisms, readily soluble in water. The *barium salt*—

$$C_6H_2Br(NH_2)\{(SO_3)_2Ba\}.8H_2O,$$

is highly deliquescent; the *lead salt* crystallises in nodules made up of fine prisms containing $3H_2O$. *Dibromamidobenzenedisulphonate of ammonium* forms dense colourless, anhydrous prisms, not readily soluble in cold water; the *potassium salt* is also anhydrous, whereas the *barium salt* contains $C_6HBr_2(NH_2)\{(SO_3)_2Ba\}.8H_2O$, and the *lead salt* crystallises in thin, flat, non-deliquescent prisms containing $3H_2O$. On passing nitrous acid into a solution of potassium α-dibromamidobenzenedisulphonate, the diazo-salt, $C_6(N_2)Br_2(SO_3H)(SO_3K)$, separates in anhydrous, microscopic, six-sided rhombic tables, but little affected by water or alcohol, but converted by hot hydrobromic acid into potassium α-tribrombenzenedisulphonate, $C_6HBr_3(SO_3K)_2$; this salt forms difficultly soluble minute prisms.

The corresponding derivatives of β-amidobenzenedisulphonic acid have not yet been examined. C. R. A. W.

Action of Sulphuric Acid on Toluene. By H. BECKURTS (*Deut. Chem. Ges. Ber.*, x, 943—947).—The action of sulphuric acid on toluene was first investigated by Jaworsky, who obtained a toluenesulphonic acid. Engelhardt and Latschinoff then took up the subject, and found that two isomeric toluenesulphonic acids were formed by the action of sulphuric acid on toluene. Wolkow next stated that these two acids, distinguished as α- and β-, belonged to the para- and meta-series. Finally Fittig and Ramsay demonstrated that the acid designated by Wolkow as the meta-acid, is undoubtedly tolueneorthosulphonic acid.

The subject has been finally taken up by the author, who directed his chief attention to the ortho-compound, and in the first place endeavoured to find a method of obtaining a good yield of it.

Sulphuric anhydride was introduced into toluene cooled by ice, and after solution of the toluene, the product was converted into potassium salt. Toluene was also introduced into fuming sulphuric acid in small quantities at a time, with continual cooling, till no more was taken up, and the potassium salts were prepared from the solution obtained. Both salts gave with phosphorus pentachloride, besides the solid sulphochloride melting at 69° (the tolueneparasulphonic chloride), an extremely small quantity of the liquid sulphochloride. When toluene was dissolved in ordinary sulphuric acid, the liquid being warmed on the water-bath—or in fuming sulphuric acid—potassium salts were formed which furnished a good quantity of liquid chloride corresponding nearly with Wolkow's results. The liquid chloride mechanically separated from the solid was freed from the portion of solid chloride still remaining dissolved in it, by cooling to −15°, and was then converted into the amide by aqueous ammonia. By fractional crystallisation from alcohol this amide was separated from another amide existing previously with it—the one being but slightly soluble in alcohol and fusing at 153—154°, the other very easily soluble in alcohol and fusing at 104°. The amide fusing at 137° could not be isolated. There could not, therefore, have been any more of the toluenepara-sulphochloride present in the sulphochloride employed. These observations show that by the action of sulphuric acid on toluene not two but three toluenesulphonic acids are formed. The amide fusing at 153° is named the ortho-compound; that at 104°, the meta-compound. The crude liquid chloride contained 80 per cent. by the first, and 20 per cent. of the second of these compounds.

Tolueneorthosulphamide.—Crystallises from alcohol in hard heavy octahedrons, from water in delicate prisms. It is but slightly soluble in water, much more easily in alcohol. Melting point between 153—154°. By heating with hydrochloric acid in a closed tube to 150°, the amide was converted into the ammonium salt of the corresponding acid, and from this the barium salt was prepared by means of barium hydrate.

Barium Tolueneorthosulphonate $(C_7H_7SO_2)_2Ba + H_2O$. — White shining scales, easily soluble in water, less easily in alcohol.

Potassium Tolueneorthosulphonate.—Tables, very easily soluble. The sulphochloride prepared from this salt by the action of phosphorus pentachloride forms a yellow oil which does not crystallise, even when cooled by a freezing mixture, and when treated with aqueous ammonia, yields the amide, melting at 153—154°.

Toluenemetasulphamide.—Crystallises from alcohol and water in slender shining needles and scales which are very soluble in alcohol and hot water, but difficult of solution in cold water. In the pure state it melts at 104—105°. Very small quantities, even traces, of impurities depress the melting point below 100°.

Barium Toluenemetasulphonate, $(C_7H_7SO_3Ba + H_2O$.—Prepared like the corresponding ortho-compound.* From dilute alcohol and from water the above barium sulphonate separates out as a white amorphous powder. It is easily soluble in water, less easily in alcohol.

The *sulpho-chloride* is a yellow oil which does not crystallise even in a freezing mixture. By aqueous ammonia it is converted into the *amide*, crystallising in white needles and scales, and fusing at 104°. The acid termed ortho-acid is identical with the acid obtained by Hübner and Post from β-parabromtoluenesulphonic acid, and by Jenssen from para-amidotolueneorthosulphonic acid. The properties assigned, by the chemists mentioned, to the chloride, amide, and barium salt of this acid completely coincide with those of these compounds derived by the author from the ortho-acid. The acid termed meta-acid is identical with the toluene-sulphonic acid obtained by Müller from the orthobromotoluenesulphonic acid, by Pagel from the orthotoluidinesulphonic acid, and by Pechmann from the para-

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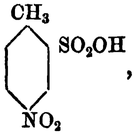
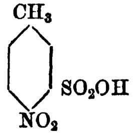
* The author observes in a foot-note that a small quantity of toluene was regenerated from both the ortho- and the meta-toluenesulphamide by heating with hydrochloric acid.—See Limpricht "Replacement of SO_3H by H" (p. 191 of this volume).

amidotoluenemetasulphonic acid. This identity was proved by coinciding properties of derived compounds as in the preceding case. The amide (Hübner and Post) melts at 90—91°; at 104° (Pagel); at 100° (Pechmann). The chloride is described by all as an oil not crystallising at −10°.
W. S.

Isomeric Sulpho-acids from Paranitro-toluene. By E. HART and IRA REMSEN (*Deut. Chem. Ges. Ber.*, x, 1046—1048).—Of the many possible modifications of nitrotoluenesulphonic acid, the following are known:—One from paranitrotoluene; one from orthonitrotoluene, which is identical with that from paratoluenesulphonic acid; and one from meta-nitroxylene. The first of these was prepared by Beilstein and Kuhlberg (*Annalen der Chem.*, clv, 11) by the action of fuming sulphuric acid on nitrotoluene; and they state expressly that only one sulpho-acid is formed during this reaction.

The authors, however (using a pure nitrotoluene), have obtained and separated two isomeric acids, or rather their calcium salts.

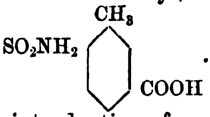
The first of these salts, containing four molecules of water, separates immediately from the concentrated solution in long slender needles; the other containing six molecules of water, is deposited on long standing in the form of monoclinic prisms. As it has been shown that the known sulpho-acid has the constitution , the only formula which remains for the second modification is—



G. T. A.

Oxidation of the Sulpho-acids of Metaxylene. By M. W. ILES and IRA REMSEN (*Deut. Chem. Ges. Ber.*, x, 1042—1046).—The difficulty of preparing pure xylene in large quantities was avoided by converting a tolerably pure coal-tar xylene into sulpho-acids, and these into the corresponding sulphamides, which could be separated by fractional crystallisation.

The authors find that three well-characterised sulphamides can be obtained from ordinary xylene, which melt respectively at 132°, 110°, and 143°. Some indications of a fourth amide were also found.

The first sulphamide, melting at 132°, is completely burnt away on oxidation. The second, melting at 110°, yields a monobasic acid—*sulphamine-metatoluic acid.* The fact that only one methyl-group undergoes oxidation, shows that the sulphamine group is not symmetrically situated with regard to the two methyl-groups in the molecule, but occupies the ortho-position with respect to one, and the para-position with respect to the other. There can be little doubt that it is the para-methyl which is oxidised into carboxyl, so that the formula of sulphamine-metatoluic acid is 

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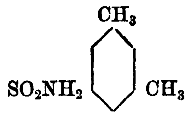
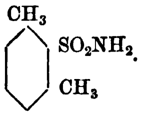
It is perhaps possible, by the introduction of carboxyl into the place of the sulphamine-group, to prepare xylidic acid.

The first amide melting at 132° is either—



or



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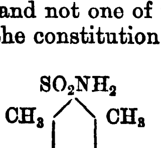
The investigation of these amides, including the third and fourth (?), will be continued. G. T. A.

Oxidation of Mesitylene-sulphonic Acid. By L. B. HALL and IRA REMSEN (*Deut. Chem. Ges Ber.*, x, 1039—1042).—Remsen has shown that the two isomeric toluene-sulphonic acids behave differently towards oxidising agents—the para-acid being converted into parasulpho-benzoic acid, whilst the ortho-acid yields simply carbon dioxide and water.

Mesitylene-sulphonic acid has the constitution of both the toluene-sulphonic acids, the sulpho-group being in the ortho-position with respect to two methyl-groups, and in the para-position with respect to the third methyl-group, and these methyl-groups must exhibit a different behaviour towards oxidising agents accordingly as they occupy the ortho- or the para-position. As potassium mesitylene-sulphonate when fused with potash exchanges a methyl-group for carboxyl, it was to be expected that the sulpho-acid itself would on oxidation be converted into an acid containing carboxyl, and such was found to be the case. For convenience the sulpho-acid was first converted into the corresponding sulphamide. The body obtained on oxidation melts at 247°. It possesses acid properties; is easily soluble in alcohol and ether, and nearly insoluble in cold water. Its most characteristic compound is the copper salt, which consists of groups of fine blue needles. These crystals lose water over sulphuric acid after they have been fully air-dried, but quickly take up the water again on exposure to air. Exposure to air at 200° produces no increase in weight. The anhydrous salt is of a bright-green colour. The formula of the hydrated salt is $(C_6H_2(SO_2NH_2)(CH_3)_2COO)_2Cu + 4H_2O$.

Since mesitylene-sulphonic acid on oxidation has only one methyl-group converted into carboxyl, it is in all probability the para-methyl which undergoes oxidation, and not one of the ortho-groups.

The amidated acid has the constitution expressed by the following formula:—



and is *parasulphamine-mesitylenic acid.*

This acid can be converted into mesitylenic acid by heating for a few hours to 200° in a sealed tube with concentrated hydrochloric acid.

The authors have prepared mesitylene from coal-tar oil, and found Jacobsen's method of separation (*Annalen der Chem.*, clxxxiv, 179) to answer very well. Further communications on mesitylene-sulphonic acid will be published shortly. G. T. A.

Action of Bromine on Triamidophenol in presence of Water. By H. WEIDEL and M. GRUBER (*Deut. Chem. Ges. Ber.*, x, 1137—1152).—As Schmitt and Bennewitz had obtained orthodichlorazophenol from orthoamidophenol by the action of chlorine, it seemed probable that a new class of azo-compounds might be obtained from the higher amido derivatives by similar means. This, however, was not found to be the case with triamidophenol. On gradually adding bromine (90 c.c.) to a solution of triamidophenol hydrochloride (200 grams) in 50 parts of water, the blue colour of the diimidoamidophenol first produced passes into yellow, and on allowing the filtered solution to stand, impure *bromodichromazin* is deposited in glistening brownish-yellow needles. The mother-liquors yield a little more of the substance on agitation with ether. It is purified by washing with boiling chloroform, and crystallising the residue from alcohol, with the aid of animal charcoal. The long yellow prismatic crystals formed on spontaneous evaporation of the alcoholic solution have been measured, as also most of the other crystalline compounds mentioned in this paper; they exhibit a feeble violet dichroism. It is very slightly soluble in ether, and insoluble in benzene, chloroform, and carbon bisulphide; boiling alcohol and acetic acid dissolve it with facility. When heated it is decomposed without previous fusion, giving off bromine vapour. The results of ten analyses lead to the formula $C_{18}H_8N_3Br_{11}O_7$ for this substance. It dissolves in concentrated sulphuric acid, but is precipitated by water unchanged, so that it is evidently not a hydrobromide of a compound of the formula $C_{18}H_7N_3Br_{10}O_7$.

Mercuric acetate, added to a solution of bromodichromazin in acetic acid or alcohol produces a pale-yellow crystalline precipitate of *mercury-bromodichromazin*, $C_{18}Hg_7N_3Br_{11}O_7 + 3Hg(C_2H_3O_2)_2$. Heated to 100°, it becomes brown, and evolves bromine, and at a somewhat higher temperature explodes. It is decomposed by sodium amalgam, with formation of ammonia, and when fused with potassium hydrate yields only oxalic acid.

Bromodichromazin, when boiled with a mixture of equal parts of sulphuric acid and water until it no longer separates on dilution, is converted into *bromodichroic acid*, $C_{18}H_7Br_{11}O_{11}$, which separates in crystalline crusts on long standing, the reaction being $C_{18}H_7Br_{11}N_3O_7 + 4H_2O = C_{18}H_7Br_{11}O_{11} + 3NH_3$. A further quantity may be obtained on extracting the acid liquors with ether. It may be purified by repeated crystallisation from a mixture of ether and benzene with the aid of animal charcoal; it then forms colourless tabular prismatic crystals of considerable size, which are easily soluble in water, alcohol, and ether. When heated they decompose below 100°, turning brown, and at a higher temperature evolve bromine, and char without previously melting. Its solution has an acid bitter taste, and easily decomposes carbonates. Bromodichroic acid yields precipitates with lead and silver salts, but they rapidly decompose, being transformed into the bromides; alkalis also decompose it very rapidly. The authors have succeeded in obtaining the calcium and barium salts by acting on their respective carbonates with a solution of the acid. They crystallise in slender needles, which are very hygroscopic, and quickly undergo change on contact with the air. Bromodichroic acid is reduced by sodium amalgam; but the authors were not able to obtain the product in a pure state, although they found that it yielded acetic acid and resorcin when fused with potassium hydrate.

When bromodichromazin is boiled for some time with dilute nitric acid, it is changed into an oil having the composition of *hexbromacetone*, C_3Br_6O, which crystallises on standing, whilst bromine and bromopicrin are produced at the same time. Chromic acid or chromic mixture acts in a similar manner; but an alkaline solution of permanganate completely decomposes it. Bromine acts strongly on bromodichromazin suspended in water, causing an evolution of carbonic anhydride, and although the action goes on slowly at the ordinary temperature, it may be completed in a few minutes by heating the mixture at 100°. On cooling, the hexbromacetone above mentioned separates in lustrous scales, which may be purified by crystallisation from chloroform. It may of course be prepared directly from triamidophenol by the action of excess of bromine, and this is the most convenient way when considerable quantities are required. It crystallises in large, colourless, highly refractive prisms, which melt at 107—109°. At a higher temperature it decomposes, only a small portion subliming unchanged. It is insoluble in water, easily soluble in ether, benzene, chloroform, and alcohol, but is decomposed by the latter. When boiled with a dilute solution of an alkaline hydrate, it yields bromoform and an alkaline carbonate, $C_3Br_6O + 2NaOH = 2CHBr_3 + Na_2CO_3$. It is decomposed in a similar manner when heated with water at 180°. It dissolves in boiling nitric acid, and separates again unchanged on cooling; but when the two are heated to 150°, bromopicrin is formed, together with carbonic anhydride and nitric peroxide, the reaction being $C_3Br_6O + 4HNO_3 = 2CBr_3(NO_2) + N_2O_4 + CO_2 + 2H_2O$*.

As Cloez found that the action of ammonia on pentabromacetone gave rise to bromoform and dibromacetamide, it seemed probable that hexbromacetone when similarly treated would yield tribromacetamide, $C_2Br_3O.NH_2$; such was found to be the case, the reaction taking place quantitatively when dry ammonia is passed over hexabromacetone in a tube. The crystalline product, when purified by crystallisation from dilute alcohol with aid of charcoal, forms white plates resembling benzoic acid, which melt at 119—121°. Large prismatic crystals may be obtained, however, by the spontaneous evaporation of its solution in benzene. It melts under boiling water, in which it is only slightly soluble; it is easily soluble in alcohol or ether, and in boiling benzene and chloroform. Tribromacetamide cannot be distilled unchanged, although it may be volatilised in a current of an indifferent gas. Alkaline solutions resolve it into bromoform and ammonia, with formation of an alkaline carbonate. Boiled with slightly diluted sulphuric acid (3 acid to 2 water) it yields ammonium sulphate and tribromacetic acid, $C_2Br_3O.NH_2 + H_2O = C_2Br_3O.HO + NH_3$. The crystals of the tribromacetic acid which separate on cooling, melt, after crystallisation from ether, at 128—130°, and are in all respects identical with the substance described by Schaeffer (*ibid.*, iv, 282). With alkalis it yields bromoform and a formate.

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* This equation is wrong: the quantities of oxygen on the two sides do not agree.—ED.

On dissolving hexbromacetone in pure methyl alcohol, adding water until the bromacetone begins to separate, and then treating the mixture with sodium amalgam, a powerful reaction takes place, and pseudopropyl alcohol is produced. It may be separated by fractional distillation, and then boils at 85°. These reactions of the compound C_3Br_6O conclusively prove that it is really hexbromacetone, $CBr_3.CO.CBr_3$. Its formation from bromodichromazin may be represented by the equation—

$$C_{18}H_8N_3Br_{11}O_7 + 34Br + 14H_2O = 3C_3Br_6O + 3NH_4Br + 9CO_2 + 24HBr.$$

The constitution of bromodichromazin is at present unknown, but the author suggests that both it and bromodichroic acid are probably closely related to the compounds which Stenhouse obtained by the action of chlorine and bromine on pyrogallol. One of these compounds, mairogallol, $C_{18}H_7Cl_{11}O_{11}$, appears to be analogous to bromodichroic acid, $C_{18}H_7Br_{11}O_{11}$, whilst bromodichromazin, $C_{18}H_8N_3Br_{11}O_{11}$, is perhaps an azo-compound. C. E. G.

Note on Sordidin. By E. PATERNÒ (*Gazzetta chimica italiana*, vii, 281—284).—In a former paper the author noticed that the lichen *Zeora sordida* contained, besides usnic acid, two other compounds, zeorin, melting at 230°, and sordidin melting at 180° (this *Journal*, 1876, ii, 203). They were obtained from the ethereal extract by fractional crystallisation from alcohol, after the bulk of the usnic acid had been separated. The cold alcohol which had been employed to wash the extract in order to remove the resin, deposited, on standing, crystals which were suspected to be sordidin, but after purification were found to melt at 210°. The residue from a large quantity of usnic acid was therefore carefully examined; it contained—besides some usnic acid—zeorin, sordidin, and brown resin. It was washed, first with ether and then with alcohol to remove the resin, and the residue fractionally crystallised from chloroform, alcohol, and benzene. In this way it was separated into usnic acid, zeorin, and a substance of the formula $C_{13}H_{10}O_8$, melting at 210°, identical with that above described. From these results it would seem, either that in the lichen last examined, the sordidin had been replaced by the compound melting at 210°, which was also present in small quantity in the sample first examined, or, what was more probable, that the first specimen of sordidin obtained was impure, and that its true melting point was 210°. This latter supposition seemed the more likely, as an attempt to prepare sordidin from the second sample of lichen by crystallisation alone, yielded a product of lower melting point. All doubts were removed by the behaviour of the substances with a boiling solution of potassium hydrate. Zeorin is unaltered by this reagent, whilst the compound melting at 210° yields a product which crystallises in slender microscopic needles which do not melt at 250°, but char at a somewhat higher temperature. On submitting a small sample of the sordidin previously described and analysed, to similar treatment, it gave the crystals melting at 250°, and zeorin. The true melting point of sordidin, therefore, is 210°, and its empirical formula $C_{13}H_{10}O_8$. The yield obtained from the lichen amounted to only 0·1 per cent.

C. E. G.

Oxidation of Cholesterin by Potassium Permanganate. By LATSCHINOFF (*Bull. Soc. Chim.*, xxvii, 456).—The oxidation of cholesterin by potassium permanganate gives rise to three different acids—cholesteric acid, $C_{26}H_{42}O_4$; oxycholesteric acid, $C_{26}H_{42}O_5$; and dioxycholesteric acid, $C_{26}H_{42}O_6$. All, except the alkaline salts of these acids, are precipitated. The salts of the first acid dissolve in alcohol, ether, and benzene; those of the second in ether and benzene, but not in alcohol; those of the third in benzene, but not in ether and alcohol.

R. R.

A Nitro-derivative of Paraoxybenzoic Aldehyde. By G. MAZZARA (*Gazzetta chimica italiana*, vii, 285—286).—The aldehyde prepared by Reimer and Tiemann's method was heated with nitric acid diluted with five times its volume of water, and the brownish-black crystalline product was freed from oily matter as far as possible by pressure between filter-paper, and purified by crystallisation from alcohol with aid of animal charcoal. It forms long yellowish needles, which melt at about 140°, and are soluble in alcohol and in boiling water, only slightly soluble in ether, chloroform, and benzene. Its aqueous solution gives a red coloration with ferric salts. Nitroparaoxybenzoic aldehyde, $C_6H_3(NO_2)(OH).COH$, easily decomposes carbonates. The potassium compound $C_6H_3.NO_2.OK.COH + H_2O$, crystallises in magnificent plates of golden-yellow colour; they give off their water at 70°. The silver compound, $C_6H_3.NO_2.AgO.COH$, falls as a canary-yellow precipitate on adding silver nitrate to a solution of the potassium compound. C. E. G.

Three Dichlorobenzoïc Acids. By R. SCHULTZ (*Liebig's Annalen*, clxxxvii, 260—274).—Monochlorotoluene, the first product of the action of chlorine on toluene in presence of iodine, has been regarded by some chemists as the *para*-compound, mainly or exclusively. If this view were correct, it would follow that the substance is capable of yielding only two dichlorotoluenes when subjected to the further action of chlorine. But the author of the present paper shows that the dichlorotoluene thus formed is a mixture of at least three (and probably *only* three) isomerides, and that consequently monochlorotoluene is not a single product.

Dichlorotoluene, obtained by passing chlorine into dry warm toluene containing molybdenum pentachloride, was purified by distillation and then converted into dichlorobenzotrichloride, $C_6H_3Cl_2CCl_3$, by the action of chlorine on its vapour. The latter product, when heated to 200° with water in sealed tubes, yielded dichlorobenzoic acid, in accordance with the equation—

$$C_6H_3Cl_2.CCl_3 + 2H_2O = C_6H_3Cl_2.COOH + 3HCl.$$

This acid, after neutralisation with barium hydrate, yielded by fractional crystallisation the barium salts of the three following acids:—

1. An acid melting at 201°, and crystallising from water in needles, identical in its properties and in those of its barium salts with Beilstein's α-dichlorobenzoic acid.

2. An acid melting at 156°, crystallising from water in delicate needles, and subliming in small laminæ, apparently identical with the β-dichlorobenzoic acid of Beilstein, Claus, and Thiel.

3. An acid melting at 126·5°, distinguished by the author as γ-dichlorobenzoic acid. It dissolves sparingly in water, more freely in alcohol, and crystallises from the latter in small needles.

The *barium salt*, $(C_6H_3Cl_2COO)_2Ba + 3\frac{1}{2}$ aq., crystallises from alcohol in stellate groups of small needles.

The *potassium salt*, $C_6H_3Cl_2COOK + 5$ aq., crystallises from water, in which it is very freely soluble, in beautiful needles.

The *ammonium salt*, $C_6H_3Cl_2COONH_4 + 1$ aq., crystallises in fine needles.

The *zinc salt*, $(C_6H_3Cl_2COO)_2Zn + 1\frac{1}{2}$ aq., crystallises indistinctly. On boiling a concentrated solution the salt is deposited, but redissolves on cooling. The zinc salt of the β-acid behaves in the same manner, but not that of the α-acid.

The *chloride*, $C_6H_3Cl_2COCl$, obtained by distilling the barium salt with phosphorus pentachloride, is a clear liquid boiling without decomposition at 244°.

The *amide*, $C_6H_3Cl_2CONH_2$, formed by the action of alcoholic ammonia on the chloride, crystallises from alcohol and water in very fine white needles melting at 166°. J. R.

Nitrobenzoic Acids. By LEO LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 1036—1038).—Three isomeric nitrobenzoic acids may be obtained by nitration of benzoic acid. The melting point of these acids, when mixed, varies, but generally lies between 115—120°. The fourth acid described by Fittica (*Berichte*, x, 481), and melting at 127°, does not exist. Mixtures of organic acids behave like metallic alloys with respect to their melting points. Thus a mixture of equal parts of oxybenzoic and paroxybenzoic acids melts between 143° and 152° (melting point of oxybenzoic acid = 200°, of paroxybenzoic acid = 210).

A mixture of equal parts of oxybenzoic acid and salicylic acid melts at 126° to 134° (melting point of salicylic acid = 155°). Several other instances are given, and these tend to show that mixtures of the known nitrobenzoic acids may give rise to others with melting points lower than those of either constitutent, which are not, however, distinct acids. G. T. A.

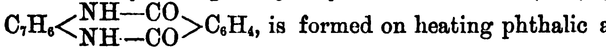
Nitrobenzoic Acids. By E. WIDNMANN (*Deut. Chem. Ges. Ber.*, x, 1159—1160).—This contains the author's determinations of the melting points of the three nitrobenzoic acids, and of mixtures of the same:—

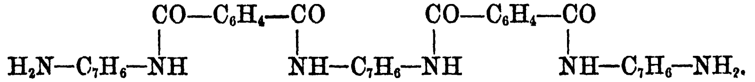
Orthonitrobenzoic acid	149°
Metanitrobenzoic acid..........	140°—141°
Paranitrobenzoic acid..........	238°

A mixture of the three isomeric acids began to melt at 137°, and was completely melted at 180°. In the following table, when two temperatures are given, the lowest indicates the commencement, and the highest the completion, of the fusion:—

Proportions in mixture.	Ortho and Meta.	Ortho and Para.	Meta and Para.
10 : 10	92°—98°	200°	165°—205°
10 : 5	125°	142°—190°	127°—185°
10 : 1	140°	141°	130°—155°
10 : 0·5	144°	145°	132°—133°
10 : 0·2	146°	147°	134°—135°
10 : 0·1	146°	145°	135°—136°
0·1 : 10	132°—135°	233°—237°	236°—238°
0·2 : 10	132°—134°	228°—235°	232°—237°
0·5 : 10	132°—140°	222°—235°	215°—234°
1 : 10	132°—133°	200°—225°	205°—230°
5 : 10	112°	210°—216°	195°—208°

C. E. G.

Action of Phthalic Anhydride on Aromatic Diamines. By R. BIEDERMANN (*Deut. Chem. Ges. Ber.* x, 1160—1166). The author finds that the action of phthalic anhydride on diacid bases is similar to that which takes place with succinic anhydride and metaphenylenediamine, namely, that the acid residue does not enter into the benzene nucleus of the aromatic diamene; but that condensation takes place, with elimination of hydrogen from the NH_2 groups in the latter. In this way *monophthalyl-tolylenediamine* $C_7H_6(NH)_2(CO)_2C_6H_4$, or  $C_7H_6{<}\genfrac{}{}{0pt}{}{NH-CO}{NH-CO}{>}C_6H_4$, is formed on heating phthalic anhydride and tolylenediamine (m.p. 99°) together until water ceases to be given off. The product is exhausted with boiling alcohol, and the residue crystallised from dry acetic acid. The yellow silky needles, which separate from the alcoholic solution, are the monophthalyl compound. After repeated crystallisation from nitrobenzene, they melt at 192°. Boiled with soda solution, or with concentrated hydrochloric acid, is is resolved into phthalic acid and tolylenediamine. The portion which it insoluble in alcohol, but crystallises from acetic acid, is *diphthalyl-tolylenediamine* $C_7H_6[N(CO)_2C_6H_4]_2$. It is insoluble in alcohol, and separates from its solution in boiling acetic acid in small, snow-white, glistening crystals, which melt at 230—233°. It is only slowly attacked by soda solution, and not at all by hydrochloric acid. If the mixture of the anhydride and the diamine be heated with phosphoric anhydride, or if the hydrochloride be substituted for the base, the same result is obtained as that above described; but on boiling the two in alcoholic solution, and then evaporating to dryness, nothing but monophthalyl-tolylenediamine is formed. The latter, when boiled with dilute hydrochloric acid, is not at once resolved into phthalic acid and tolylenediamine, but an intermediate product is first formed of the formula,



$$\begin{array}{lll} & \mathrm{CO{-}C_6H_4{-}CO} & \quad \mathrm{CO{-}C_6H_4{-}CO} \\ & | \qquad\qquad\quad | & \quad | \qquad\qquad\quad | \\ \mathrm{H_2N{-}C_7H_6{-}NH} & \mathrm{NH{-}C_7H_6{-}NH} & \quad \mathrm{NH{-}C_7H_6{-}NH_2}. \end{array}$$

the liberated phthalic acid acting on another molecule of the monophthalyl-tolylenediamine, to form the compound

$$C_7H_6[N{=}(CO)_2{=}C_6H_4]_2$$

above mentioned. The hydrochloride of the base crystallises in beautiful rhombic plates, and gives a reddish-yellow platinum salt $C_{37}H_{32}N_6O_4$ (HCl.)$PtCl_4$. The base itself is very soluble in water, and difficult to purify.

The action of phthalic anhydride on para- and metaphenylenediamine takes place in a manner precisely similar to that with the tolylenediamine. *Diphthalylparaphenylenediamine* $C_6H_4[N(CO)_2C_6H_4]_2$, crystallises from acetic acid in needles which melt at 295°. The *monophthalylparaphenylenediamine* $C_6H_4(NH)_2(CO)_2C_6H_4$ is a crystalline powder melting at 182°. *Diphthalylmetaphenylenediamine* melts at 252°, and the *monopthalyl*-compound at 178°. The reactions of these compounds with alkaline solutions and with acids are strictly analogous to those of the compounds previously described.

Two compounds, melting at 104° and 272°, have been obtained by the action of phthalic anhydride on tolylenediamine melting at 80°. All the compounds described yield nitro derivatives, and yellow nitroso-compounds have been obtained from the bases. The author concludes the paper by stating that phthalic anhydride and urea fused together yield phthalimide, with evolution of ammonia and carbonic anhydride, whilst, if boiled in alcoholic solution, a molecular combination of phthalic acid with urea is formed. C. E. G.

Oxyphthalic Acid. By A. BAEYER (*Deut. Chem. Ges. Ber.*, x, 1079—1084).—The ethyl amidophthalate employed in this research was prepared by saturating an alcoholic solution of crude nitrophthalic acid with dry hydrochloric acid, separating the ethyl nitrophthalate thus formed by the addition of water, and after washing it with a solution of sodic hydrate, dissolving it in alcohol, and reducing it by means of hydrochloric acid and zinc powder. By this means crystallised ethyl amidophthalate was obtained equal to 80 per cent. of the theoretical for the amount of ethyl nitrophthalate employed.

The ethyl amidophthalate was converted into oxyphthalate by dissolving it in dilute sulphuric acid (40 parts), and after decolorising the solution by means of animal charcoal, gradually adding a solution of sodium nitrite, and heating to 100°. Great care must be taken not to employ excess of the nitrite, or yellow compounds will be formed, which greatly diminish the yield of the oxyphthalate. The ethyl oxyphthalate separates as an oil, which is soluble in alkaline solutions, and is reprecipitated by acids; it does not crystallise, neither does it volatilise without decomposition. The ether was saponified by boiling with a concentrated solution of potassium hydrate, and the acid precipitated as lead salt: the latter suspended in water and decomposed by sulphuretted hydrogen, gave a colourless solution, from which the oxyphthalic acid was extracted by concentration and agitation with ether. *Oxyphthalic acid*, $C_8H_6O_5$, or $C_6H_3(OH)(COOH)_2$, obtained by dissolving the anhydride in boiling water, and allowing the solution to cool, crystallises in tufts, which are readily soluble in hot water, but require 32·4 parts at 10°. It is very soluble in alcohol and acetone, less so in ether, and is almost insoluble in the hydrocarbons. It melts at about 180°, being resolved into water and the anhydride. The salts which oxyphthalic acid forms with the alkalis and alkaline earths are very soluble. Ferric chloride gives a reddish-yellow colour with the acid. When oxyphthalic acid is heated with concentrated sulphuric acid for four hours at 200°, and the dark-coloured product poured into water, a greenish-yellow precipitate is formed, from which three distinct substances have been obtained:—1. A yellow sublimable body, resembling anthraflavone. 2. A substance resembling a phthalideïn, soluble in sulphuric acid with a splendid red colour. 3. A colourless crystalline compound, which melts at 123°, and sublimes unchanged. Oxyphthalic acid in aqueous solution is easily reduced by sodium amalgam, but the product (presumably hydroxyphthalic acid) has not been examined.

Oxyphthalic anhydride, $C_8H_4O_4$, is formed when the acid is heated at 180°. It sublimes unaltered at 200—210°, in long needles, totally different in appearance from those of phthalic anhydride, but it cannot be distilled unchanged. The anhydride melts at 165—166°, and when heated with aniline, at 160—180°, yields a well crystallised anilide.

An *oxyphthaleïn of phenol*, which very closely resembles the corresponding phthaleïn, is formed on heating the anhydride with phenol and sulphuric acid, at 115°. It is somewhat more soluble in water than the phthaleïn, and its dilute alkaline solution is rose-red. It is reduced by zinc-dust to a colourless oxyphthalin, which, by the action of concentrated sulphuric acid, is converted into a greenish-yellow oxyphthalidin; the latter, like the phthalidin, is oxidised by sulphuric acid and manganese peroxide in the cold, yielding a colourless oxyphthalideïn, which dissolves in sulphuric acid, with a blue violet colour. Oxyphthalic anhydride heated with resorcin at 200°, yields *oxyfluoresceïn*, resembling fluoresceïn in every respect, and the brominated derivative resembles eosin, but gives a somewhat redder shade on silk. The *oxygalleïn* is also very similar to galleïn.

The author concludes with some theoretical considerations. The hydroxyl group in oxyphthalic acid may occupy two different positions, but this question is at present undetermined, the formation of meta-amidobenzoic acid from amidophthalic acid by boiling it with hydrochloric acid yielding no information. Perhaps the study of the second nitrophthalic acid indicated by O. Miller (*ibid.*, x, 709), may throw some light on the matter. As oxyphthalic acid so closely resembles phthalic acid in its reactions with resorcin, the formation of a fluoresceïn will serve to distinguish it from isomeric derivatives of isophthalic and terephthalic acids. C. E. G.

A new Acid (Atranoric Acid) from Lecanora atra. By E. Paternò and A. Ogliatoro (*Gazzetta chimica italiana*, vii, 189—192). The ethereal extract of this lichen, collected in the neighbourhood of Palermo, yielded, on evaporation, a crystalline mass mixed with a soft brown resin, which was easily removed by washing with cold ether. The crystals are a mixture of two acids, which were separated by means of chloroform; one (*atranoric acid*) is colourless, and but slightly soluble in cold chloroform; whilst the other, which is yellow, is very soluble.

Atranoric acid crystallises from chloroform in small, colourless, transparent prisms, which melt at 190°, and are only very slightly soluble in cold alcohol or ether; it is moderately soluble in boiling chloroform. The results of the analysis correspond closely with the formula $C_{19}H_{16}O_8$. It has feeble acid characters, although it does not affect litmus, dissolving in alkaline solutions, and being reprecipitated by acids. Boiled with aniline and alcohol, it yields a compound crystallising in lustrous yellow needles, which melt at 156°. Heated with alcohol at 150°, it is converted into a crystalline substance, very soluble in alcohol. It forms long needles, which melt at 115°.

The yellow acid accompanying atranoric acid in this lichen, closely resembles usnic acid in appearance, general characters, and behaviour with solvents, but melts at 175°, whilst usnic acid melts at 195—197°. Heated with alcohol at 150°, it yields a substance crystallising in slender needles, and melting at 175° just like the decarbusnic acid obtained from usnic acid by this process. With aniline and alcohol it also behaves like usnic acid. The product of the dry distillation of the acid, when extracted with water and filtered from tar, gives a yellow colour with ammonia and potash, brown with ferric chloride, and deep red with sodic hypochlorite. Usnic acid (from *zeora sordida*), gives results almost identical. This would tend to show that the acid is merely usnic acid whose melting point is lowered by the presence of some impurity in small quantity; the results of the analysis give carbon about 0·5 per cent. lower than that required by the formula $C_{18}H_{16}O_7$. The author suggests that the beta-usnic acid of Hesse, and the cladonic acid of Stenhouse, extracted from *Cladonia rangiferina*, may be merely impure usnic acid.

The authors have also obtained, from a variety of the same lichen, (*Lecanora atra panormitana:* De Notaris), another acid, melting at 91°, and which they propose to call *atralinic acid.* Its formula is $C_{16}H_{18}O_5$.

Appended to this paper is a note by Paternò, in which he refers to a substance, described in his memoir as usnate of aniline, obtained by boiling usnic acid with aniline: It crystallises in yellow needles, melting at 142°, and was considered to be an usnate of aniline. He now finds that, on boiling the acid with excess of aniline, another compound is produced, which crystallises in leafy plates, melting at

170°, and much less soluble in alcohol than the compound previously described. It is not an usnate of aniline, but it is at present under investigation. C. E. G.

Isolepidene. By M. ZININ (*Bull. Soc. Chim.*, xxvii, 546).—Isolepidene forms rather more than a third of the weight of oxylepidene submitted to distillation, and is always accompanied by a considerable quantity of oxylepidene. Treated with a mixture of zinc and acetic acid, isolepidene fixes two atoms of hydrogen, whilst the action of sodium amalgam on an alcoholic solution gives rise to an addition-product with four atoms of hydrogen. The oxidation of isolepidene by chromic anhydride produces at first an isomeride of oxylepidene, but afterwards the product is benzophenone. Benzoic acid and benzile are secondary products of the reaction. R. R.

Anthraquinone. By A CLAUS (*Deut. Chem. Ges. Ber.*, x, 925—928).—Several years ago the author observed that by passing chlorine, or dropping bromine, into a boiling alcoholic solution of anthracene, anthraquinone was formed and crystallised out after a short time. An endeavour to base a quantitative method of determining anthracene in the crude article on this fact failed, owing to the reaction going too far or not far enough. However, the reaction did not seem to lack interest, especially as by similar treatment naphthalene cannot be converted into naphthaquinone. The reaction is very well suited as a lecture experiment. 1 gram of anthracene is treated with 4 to 6 times its bulk of alcohol in a small flask, so that on boiling, only a part dissolves, and then a rapid stream of chlorine is passed through the boiling liquid, or bromine is introduced. After cooling, the liquid is filtered, the residue on the filter washed first with cold alcohol then with dilute soda-solution, and finally after drying sublimed between watch-glasses. The chlorinised products are recognised in the sublimate by their yellow colour.

Hydroanthraquinone was obtained by Böttger and by Graebe and Liebermann, by reduction of anthraquinone with zinc-dust and sodium hydrate. It may likewise be obtained from anthraquinone by treatment with sodium-amalgam. When the latter and anthraquinone are brought together, and the mixture is treated with water, a clear deep-red solution of sodium-hydroanthraquinone is obtained after a short time. This is especially the case if violent motion of the vessel be avoided. After pouring off the excess of amalgam and leaving the residue exposed to the air, the colour disappears gradually, or on shaking with air, quickly, fine needles of regenerated quinone separating out. This is said to make an excellent lecture experiment, and also to serve for detecting the smallest traces of anthraquinone. A few particles of anthraquinone (1 mgr. is amply sufficient) are placed in a test-tube with some sodium-amalgam, and treated with absolute ether free from alcohol, the whole being well shaken for some time. If now a drop of water be let fall into the ether and the vessel gently moved, a splendid red colour appears, which immediately disappears on shaking, so as to bring the red solution in contact with the air above the ether;

on leaving it at rest the colour soon reappears. This play of colour may be repeated as often as desired by alternately shaking the liquid and leaving it at rest. If absolute alcohol be used instead of ether, there appears at the point of contact of the alcohol and sodium amalgam, a dark-green zone, which on gently shaking extends to the whole solution, turning it to a splendid green. On shaking air through however, the colour entirely disappears. This reaction may also be repeated at pleasure with the same trace of anthraquinone, if enough amalgam be present. Should the alcohol, however, contain a trace of water, then a red colour appears instead of the green, and may be made to disappear and reappear the oftener the more water is present, by shaking air through as before mentioned. This reaction is recommended as an extremely good test for the presence of water in alcohol. These colour reactions merely prove that anthraquinone is always regenerated from the coloured products on shaking with air. This fact was proved experimentally by testing the melting point and other properties of the regenerated anthraquinone. The constitution of the green body is now a subject of investigation. The author has also commenced with Schnutz the investigation of the action of zinc-ethyl on anthraquinone. By causing 4 molecules of zinc-ethyl to act on 1 molecule of the quinone, a very lively reaction is set up and a brown plaster-like mass is obtained, easily soluble in alcohol and ether. This has not as yet been crystallised. It is easily soluble in nitric acid, and from the solution water precipitates a solid nitro-product, now under examination. Ethiodide of zinc acts more gently, and furnishes the same product. Other quinones have been likewise experimented on, as benzene-quinone and naphtho-quinone. The authors hope, by the help of these reactions, to find a means of throwing light on the often repeated supposition that the bodies going under the general name of quinones are not really analogously constructed. The reaction of hydrocyanic acid, and of this acid with hydrochloric acid, on the different quinones, has also been taken in hand. W. S.

Munjistin, ε-Purpurin, and Purpuroxanthincarbonic Acid. By E. Schünck and H. Römer (*Deut. Chem. Ges. Ber.*, x, 790—792). —The authors find that the munjistin discovered by Stenhouse is identical with their purpuroxanthincarbonic acid, and that munjistin gives a crimson and not a yellow barium-lake, as first reported by Stenhouse. Stenhouse discovered the substance and named it munjistin, whilst Schünck and Römer have settled its formula, $C_{15}H_8O_6$, and its position with regard to the other colouring matters of madder. These two chemists extracted their product from "munjeet," just as Stenhouse did, and compared the results of their analyses with those executed upon purpuroxanthincarbonic acid.

With respect to ε-purpurin, Rosenstiehl has stated that this body is identical with purpuroxanthincarbonic acid. This assertion appears to the authors not a little unscrupulous, inasmuch as Rosenstiehl thus makes his ε-purpurin $2\frac{1}{2}$ per cent. poorer in carbon, without giving any numbers to justify the alteration, and apparently forgets that the melting point of ε-purpurin is 180°, whilst that of purpuroxanthincarbonic acid is 231°, a difference of more than 50°. Rosenstiehl alters the formula of his ϵ-purpurin from $C_{14}H_8O_5$ to $C_{15}H_8O_6$, but unfortunately the synthetical method of preparation suitable to the previous formula is allowed to remain. He maintains (*Compt. rend.*, lxxxiii, 829) that ϵ-purpurin is formed by the oxidation of purpuroxanthin, and this he maintains after he has given the new formula, $C_{15}H_8O_6$, to the ϵ-purpurin. It is naturally an enigma to the authors how $C_{14}H_8O_4$ (purpuroxanthin) can by simple oxidation be converted into $C_{15}H_8O_6$ (purpuroxanthincarbonic acid). Another peculiar source for ϵ-purpurin is, according to Rosenstiehl, pseudo-purpurin, to which he has lately given the formula $C_{16}H_8O_7$. By boiling with water it is said to split up into $C_{15}H_8O_6$ and $C_{14}H_8O_5$ (purpurin hydrate). The madder-orange of Runge, Rosenstiehl has declared in his last communication to be also identical with ϵ-purpurin (corresponding to purpuroxanthincarbonic acid). Only a few months ago the same chemist declared that till then only contradictory statements had appeared about this body, and if the authors understood aright, he further stated it to be a mixture of ϵ-purpurin and purpuroxanthin. However, according to the latest results of Stenhouse and Stokes, the said orange is not identical with munjistin, and the authors have further already shown that it cannot also be identical with purpuroxanthincarbonic acid. Finally, ϵ-purpurin cannot be compared with any individual chemical body, as it is undoubtedly a mixture of an unknown number of bodies. W. S.

Eterpene (Ethyl-eterpene). By F. V. Spitzer (*Deut. Chem. Ges. Ber.*, x, 1034—1036).—The author described in a former paper (this *Journal*, 1876, ii, 514) a body derived from camphor chloride by means of ethyliodide and sodium, for which the name of eterpene (= ethyl-terpene) was proposed. He now finds that the same reaction takes place at the ordinary pressure and without the use of benzene as a solvent, but that the so-called eterpene, ($C_{10}H_{15}.C_2H_5$), is a terpene, and that the ethyliodide does not take a part in the reaction. G. T. A.

The Polythiohydrates of Strychnine. By A. W. Hofmann (*Deut. Chem. Ges. Ber.*, x, 1087—1894).—Some years ago the author described a compound of strychnine obtained in yellow crystals (*ibid.*, i, 81) on mixing an alcoholic solution of strychnine with one of yellow ammonium sulphide, and to which he assigned the formula, $C_{21}H_{22}N_2O_2.H_2S_3$. Since then Schmidt (*ibid.*, viii, 1267) has obtained what he believed to be a different compound, $(C_{21}H_{22}N_2O_2)_2(H_2S_2)_3$, by passing hydrogen sulphide into an alcoholic solution of strychnine and exposing it to the air. The author has compared these two substances and finds them to be identical. The question naturally arose, which of the two formulæ given is the correct one? This evidently could not be settled by the results of the elementary analysis, as the difference in the percentage of hydrogen would fall within the limits of experimental error; recourse was therefore had to a determination of the amount of hydrogen outside the strychnine molecule. If the compound contained H_2S_2 it would, when treated with arsenious acid in hydrochloric acid, yield As_2S_6, whilst if it contained H_2S_3 it would yield As_2S_9; on making the experiment the analytical results showed that the precipitate actually contained As_2S_{18}, indicating that the strychnine compound contained H_2S_6. Similar results were obtained on heating it with lead acetate and acetic acid. It would seem therefore that the correct formula for this compound is really $(C_{21}H_{22}N_2O_2)_2.H_2S_6$. This formula agrees with the results of the elementary analysis even better than the one originally proposed by the author.

The author considers it probable that this compound has a constitution analogous to that of the periodide, $C_{21}H_{22}N_2O_2.HI.I_2$, and that it may perhaps be $C_{21}H_{22}N_2O_2.H_2S_2.S_4$, in which case the oily drops liberated on treating the substance with an acid must be regarded as a solution of sulphur in hydrogen persulphide. C. E. G.

Picrotoxin. By E. PATERNÒ and A. OGLIALORO (*Gazzetta chimica italiana*, vii, 193—197).—After referring to their former paper on this subject (this *Journal*, 1877, i, 719), in which they mentioned that the action of bromine on picrotoxin did not appear to give rise to a dibrominated derivative, as supposed by Barth, the authors state that when bromine (2 mols.) is added to picrotoxin (1 mol.) suspended in ether, hydrobromic acid is given off, and the picrotoxin is converted into a mixture of two compounds, both insoluble in ether; the same compounds are formed by the action of bromine on picrotoxin in hot aqueous solution. One of the substances contains bromine, and may be readily separated by dissolving the mixture in boiling alcohol, when it separates in the crystalline state on cooling. The analytical results agree with the formula $C_{15}H_{15}Br.O_6$, that of *monobromopicrotoxide*, if the formula previously given for picrotoxide be changed to $C_{15}H_{16}O_6$. This monobromo-derivative forms small, transparent, colourless prisms which decompose at about 240° to 250° without melting. The second substance remaining in solution in the alcoholic mother-liquors, in which it is readily soluble, may be purified by repeated crystallisation from boiling water. It crystallises in long slender needles which melt at 246—248°, but are at the same time decomposed. The numbers obtained on analysis agree with the formula $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6 + H_2O$, that of a *hydrate of picrotoxide*. If this compound be boiled with acetyl chloride for about an hour, hydrochloric acid is given off, and after removing the excess of acetyl chloride, a soft viscous mass is left which, on treatment with boiling alcohol, yields picrotoxide and a compound having the composition $C_{15}H_{16}O_7(C_2H_3O)_2$. This crystallises in thin plates which melt at 202°. Hydrate of picrotoxide also appears to be formed, together with picrotoxide, when hydrochloric acid is passed into picrotoxin suspended in ether. It possesses acid properties, and seems to stand in the same relation to picrotoxide that santonic acid does to santonin. C. E. G.

New Red Colouring Matter accompanying Chlorophyll. By C. BOUGAREL (*Bull. Soc. Chim.*, xxvii, 442, 443).—After fresh leaves of the peach-tree had been treated with ether, the liquid was poured off and alcohol substituted. Two days afterwards there were observed on the leaves and on the sides of the vessel brilliant scales of a greenish colour by reflected light, but red by transmitted light. These crystals were found to be insoluble in water, nearly insoluble in alkalis, acids, alcohol, and ether, but very soluble in chloroform and benzene, to which they imparted a beautiful rose colour. The author proposes to call this red colouring matter *erythrophyll*. R. R.

Colouring Matter of Velella Limbosa. By A. and G. DE NEGRI (*Gazzetta chimica italiana*, vii, 219).—This pelasgic mollusc, which is only rarely thrown up on the beach, gives a blue colouring matter which is readily distinguished from that of murex and aplysia by the absence of absorption-bands, when examined spectroscopically. The colouring matter is very fugitive, disappearing rapidly on the death of the animal. It is insoluble in ether, chloroform, benzene, and carbon bisulphide, but soluble in water, the solution turning yellow when heated; acids turn it red, and it is decolorised by the hypochlorites. C. E. G.

The Colouring Matter of "Boletus Luridus." By G. CUGINI (*Gazzetta chimica italiana*, vii, 209—212).—In 1860 Phipson attributed the purple colour which the freshly-cut surface of *B. luridus* and *B. cyanescens* show when exposed for a short time to the air, to aniline; the author finds, however, that the coloration is not produced by oxidation, but by the action of ammonia. The extract obtained by treating the fungus with dilute alcohol yields nothing to ether, showing that no aniline is present. The extract is strongly acid, and is coloured blue by ammonia in small quantity, although excess of the alkali destroys the colour: potassium hydrate gives a deep wine-yellow. Ferric chloride gixes a green colour, and tincture of iodine a greenish-brown colour. The author did not succeed in isolating any crystalline substance. C. E. G.

Physiological Chemistry.

On the Situation of the Deposit of Fat in Animals on different Diets. By J. FORSTER (*Zeitschr. für Biologie*, xii, 448—463).—Having premised that in an animal two causes operate in producing a reserve of fat, viz. :—(1.) The accumulation of the fat of the nourishment which reaches the organism in excess; and (2.) The formation of fat from albumin in the body, and its accumulation there in consequence of the consumption of an abundance of carbo-hydrates, the author contends that in the former case an accumulation of fat should occur in the so-called fat-tissues (subcutaneous cellular-tissue, mesentery, &c.), whereas in the latter, seeing that the formation of fat must be supposed to take place in the cells of the different organs, the fat-deposit should occur in those organs (liver, muscles, &c.) in proportion to the amount of the metamorphosis of albumin taking place in them.

To ascertain whether this difference takes place the author experimented with three pigeons, feeding them all three for six days on 5—6 grams of horse-meat, dried, powdered, and deprived of fat, together with water. The birds having lost much fat, one (A) was killed, and the amount of fat in the different parts of the body estimated. The second pigeon (B) was then fed on fat with a trace of meat-powder and killed after three days. The third pigeon (C) was at the same time fed on two parts of the meat-powder and two-and-a-half parts of starch for nine days, and then killed. An estimation of the fat in the different organs gave the following results:—Both the absolute as well as the relative content of fat was much increased in pigeons B and C. The insufficiently fed pigeon (A) contained more water in all the organs than the other two. This is a well known fact. No increase of fat had taken place in the livers of pigeons B and C. With regard to the position of the fat, the author concludes that there is *no* noticeable difference, whether the fat is derived from without, or is formed with in the animal body: both varieties of fat, at least at the commencement of fattening, become equally deposited, and in the case of the pigeon the deposit takes place principally in the subcutaneous connective tissue. This accumulation of fat at a distance from the point of its formation the author considers an additional proof of its ready passage through animal cells and membranes. E. C. B.

Loss of Lime in the Body, especially in the Bones, on an Insufficient Supply of Lime. By J. FORSTER (*Zeitschr. für Biologie*, xii, 464—474).—The author adduces some experiments on the dog, made by him in 1869, to show that with a diet containing an insufficient quantity of lime, but sufficing to sustain the albuminous constituents of the organism, all the organs, more especially the muscles, but also the skeleton, become partially impoverished in lime, without any diminution in the organic substances of the body taking place. He finds that the quantity of lime contained in a diet consisting exclusively of meat, does not suffice to sustain the amount of lime in the body, although its albuminous constituents may remain unchanged.

He explains Weiske's inability to observe, on an insufficient supply of lime, either a partial loss of lime in the skeleton, or the occurrence of disease of the bones by the following considerations:—(1.) Conclusions with regard to the composition of the whole skeleton must not be drawn from an analysis of individual bones. (2.) It is necessary that the nourishment of the animals be such that whilst losing lime they may not suffer a diminution in combustible substances. For with a generally insufficient supply of nourishment besides the want of lime, both soft parts and bones diminish, and the ash-components which are thus set free, may, under certain circumstances, be used again without being excreted from the body. E. C. B.

The Excrements of Poultry. By W. VON KNIERIEM (*Zeitschr. für Biologie*, xiii, 36—79).—The author desiring to find what effect those substances had on the excrements of birds, which were known to be converted into urea in the mammal, has carried out a series of elaborate experiments which prove that in the bodies of poultry these substances are in all cases converted into uric acid. The substances experimented upon were asparagin, aspartic acid, glycocine, leucine, and ammonium salts.

With regard to the ammonium salts, the author finds that though converted into urea in the mammalian organism, they leave the body of the fowl in their original state. This accounts for an excess of ammonia in the excrement above that necessary to combine with the uric acid present.

The author also draws the following conclusion:—During the digestion of proteids by fowls, the same bodies are formed as in the case of mammals, viz., aspartic acid, leucine, and glycocine; and these products may be regarded as the forerunners of uric acid. F. J. L.

Cystinuria. By A. Niemann (*Liebig's Annalen*, clxxxvii, 101—112).—The amount of cystine in a calculus passed by a young man who had felt no discomfort except trembling of the hands, was estimated and compared with the amounts of sulphuric acid and uric acid in the urine. The cystine was estimated by filtering off and weighing the substance which crystallised out. The mucous matter in the urine was separated by freezing and subsequent filtration. The cystine was separated from the mucus by digesting it with strong ammonia to dissolve it, and the solution was then evaporated to dryness and weighed. The maximum quantity of cystine voided *per diem* was nearly 1 gram. The angle of the crystals was measured and found equal to 120°.

The proportion of the cystine to the sulphuric and uric acids, and to the urea are given at full length in tables. The conclusion drawn from numerous comparisons is that in general the more cystine exists in urine the greater the quantity of sulphuric acid present. The average proportion of cystine to sulphuric acid is 1 : 3·9. The uric acid was present in too small quantity for satisfactory determination; the urea was present in normal or nearly normal amount. W. R.

Chemistry of Vegetable Physiology and Agriculture.

Concentration of Wine-must by Cold. By C. Neubauer (*Landw. Versuchs-stat.*, xx, 105—112).—The author states that although 1875 was a good wine year, it was remarkable for the severe weather during November, which afforded opportunity for some interesting experiments.

In the first place, results obtained by W. Rasch of Oestrich on the Rhine, are given. He states that in 1858 yellow stains were found under the vines upon snow that had fallen during very cold weather; this was produced by the water becoming partially frozen out of the grape-juice. It was of course impossible to press them in the ordinary way, so they were placed in deep tubs, with a hole at the bottom through which the juice—having a high specific gravity—ran out. A sample of this must, which was fairly fermented, gave on analysis the following results:—

Alcohol	9·62	per cent. by weight.
Free acid	0·87	,, ,,
Sugar....................	0·72	,, ,,
Extractive matter..........	2·77	,, ,,
Ash......................	0·25	,, ,,

In a tube 200 mm. long the plane of polarisation was turned 4° to the left.

The wine was unusually good, on account of the freedom from husk and woody fibre of the must from which it was prepared.

Similar experiments were made by G. Brentano of Winkeler on the Rhine. The grapes were collected at a temperature of —17·5° and submitted to strong pressure in a house at the temperature of —10°, 600 litres of very concentrated must were obtained. The author analysed specimens of the wine in April of the same year: it was somewhat muddy, and fermentation had not ceased. The results are given in the following table:—

Analyses of various first-pressed Wines; the Must obtained from frozen Grapes at — 10°.

	Alcohol by weight per cent.	Free acid, per cent.	Sugar, per cent.	Ash, per cent.	Extractive matter, per cent.	Specific gravity.	In tube 200 mm. long; the plane of polarisation was turned.
Winkeler Opferberg, No. 20	6·82	0·93	8·62	0·15	10·50	1·0243	— 9·8° L.
,, ,, No. 21	6·40	0·88	6·69	0·15	9·61	1·0233	— 9·2° L.
,, ,, No. 22	7·39	0·91	9·18	0·17	11·26	1·0328	—10·2° L.
,, ,, No. 23	8·03	0·83	5·96	0·17	8·17	1·0182	— 7·8° L.
,, Hongberg, No. 24	6·39	1·075	10·69	0·18	13·62	1·0353	—11·4° L.
,, ,, No. 25	7·35	0·89	4·79	0·15	7·74	1·0168	— 7·1° L.

The hard-frozen residue from the press was thawed and pressed a second time, when it yielded a thin wine, giving:—

Alcohol	5·43	per cent.
Free acid	0·596	,,
Ash	0·183	,,
Sugar	0·179	,,
Extractive matter	2·03	,,

In Hungary wine is prepared from sun-dried grapes, the removal of water adding to the strength of the wine produced.

The above experiments led the author to try the concentration of must by means of Meidinger's ice-machine—a sketch and description of which are given. A sample of Neroberg must from the year 1875 was used. Analysis:—

Specific gravity	1·0925	
Sugar	18·34	per cent.
Extractive matter	22·97	„
Free acid	0·735	„
Nitrogen	0·0442	„
Ash	0·322	„

For each experiment one litre of must was used, and the process stopped as soon as a layer of ice 1 centimeter thick was formed in the inner cylinder of the machine. On separating the ice, one litre of the above must, having a specific gravity of 1·0925, yielded ½ litre of a concentrated liquor, having a specific gravity 1·1575, and ½ litre of an aqueous solution, specific gravity 1·0438. In a second experiment 1 litre of must yielded ½ litre of liquor, specific gravity 1·149, and ½ litre of an aqueous solution, specific gravity 1·049. No doubt better results would be obtained on the large scale. The concentrated must gave on standing large quantities of argol, by which the amount of free acid was greatly reduced.

Both liquids were then fermented at high summer temperatures, when they became clear, and the analyses of the resulting wines gave:—

	No. 1 Wine, obtained from the Neroberg Must, concentrated by cold.	No. 2 Wine, obtained from the thawed ice.
Specific gravity	1·0644	—
„ of the wine without alcohol	1·0785	—
Alcohol, per cent.	8·55	4·40
Free acid „	1·13	0·45
Sugar „	13·94	·0
Extractive matter, per cent.	18·33	1·456
Ash „ „	0·693	0·125

These results clearly show the value of the concentration process, the wine obtained from the concentrated must being nearly equal in quality to that of the best vintages, whereas the liquid obtained from the thawed ice scarcely deserved the name of wine. R. C. W.

Composition of Yam Tubers. By J. MOSER (*Landw. Versuchs-stat.*, xx, 113—115).—The tubers—*Dioscorea edulis*—were raised in Northern Italy. The milky juice obtained from them gave on extraction with ether, alcohol, and an alcoholic solution of carbon bisulphide, a fatty substance, together with gum of an elastic nature, having a disagreeable taste, and behaving like caoutchouc when heated. The tubers, which were somewhat shrivelled through loss of water, gave on analysis:—

	On original.	On dry.
Water	60·722	—
Ash, free from C, CO_2, and SiO_2	0·895	2·278
Protein compounds	4·485	11·419
Extract with ether	0·348	1·561
,, alcohol and an alcoholic solution of carbon bisulphide	0·265	
Cane sugar	4·790	12·195
Levulose	0·180	0·458
Starch	25·185	64·121
Pectin and other non-nitrogenous extractive matters	2·033	5·176
Fibre	1·094	2·785
Sand	0·033	0·007

The pure ash gave:—

K_2O	47·490
Na_2O	10·636
CaO	13·354
MgO	3·433
Fe_2O_3	0·695
P_2O_5	9·987
SO_3	3·550
SiO_2	0·853
Cl	12·450
	102·448
After deducting O for chlorine present	2·810
	99·638

The amount of CO_2 in the ash freed from C and SiO_2 was 16·702 per cent.

The tubers could not be used for the production of starch, as it was found impossible to obtain this substance free from the gum above alluded to.

R. C. W.

Occurrence of Oxalic Acid in Fungi. By W. M. HAMLET and C. B. PLOWRIGHT (*Chem. News*, xxxvi, 93).—The authors mention that the presence of oxalic acid in the form of hydro-potassic oxalate or calcium oxalate has been regarded by some chemists as a common constituent of fungi—a fact which is more fully proved by the investigations of the present paper. The authors observed some time ago that various specimens of *Peziza venosa*, Pers., a large number of *Hymenomycetes*, *Lycoperda*, and *Sphaeriæ* gave a strong acid reaction to litmus-paper. The question naturally presented itself as to what free acid or acid salt could be so widely distributed in the fungus tribe, when, on further examination, a marked reaction for oxalic acid was obtained. Amongst a great number of experiments, one of the most remarkable examples of strong acidity was that of *Fistulina hepatica*, which contained 0·083 p. c. of free acid. The following is the result of a proximate analysis of this plant:—

Water			86·120
Volatile constituents	Oxalic acid	0·08	12·984
	Fat	0·15	
	Woody fibre (cellulose)	2·03	
	Mycose		
	Extractive matter		
	Resin		
Mineral constituents ash)	Silica		0·896
	Ferric oxide		
	Lime		
	Magnesia		
	Potash		
	Phosphoric acid		
	Sulphuric acid		
	Chlorine		—
			100·000

The presence of oxalic acid was found in the following species:—*Agaricus (Amanita) phalloïdes*, Fr.; *rubescens*, Pers.; *vaginatus*, Bull. *Agaricus (Lepiota) procerus*, Scop.; *Agaricus (Clitocybe) maximus*, Fr.; *baccatus*, Scop.; *Agaricus (Mycena) galericulatus*, Scop.; *Agaricus (Hypoloma) appendiculatus*, Bull.—*Lactarius rufus*, Fr.; *subdulcis*, Fr.; *torminosus*, Fr.—*Russula vitellina*, Fr.—*Cantharellus cibarius*, Fr.; *aurantiacus*, Fr.—*Panus torulosus*, Fr.—*Boletus luteus*, Fr.; *scuber*, Fr.—*Polyporus betulinus*, Fr.; *rubescens*, Fr.; *farinellus*, Fr.—*Fistulina hepatica*, Fr.—*Lycoperdon giganteum*, Batoch.; *gemmatum*, Fr.—*Leotia lubrica*, Pers.; *Peziza venosa*, Pers.; *rutilans*, Fr. From these and other facts, the authors conclude that all mature non-microscopic fungi contain oxalic acid, either free or combined. D. B.

Analyses of Dried Fruits. By J. BERTRAM (*Landw. Versuchs-stat.*, xix, 401—412).—

	Stones or stalk.	Pulp.	Water.	Albumin.	Fibre.	Extract free from N.	Grape sugar.
Plums	13·70	86·30	30·03	1·31	1·34	52·44	42·28
Pears	1·37	98·63	29·61	1·69	7·18	58·35	29·39
Apples	—	—	32·42	1·06	5·59	58·97	39·71

	Cane sugar.	Starch.	Free acid.	Pectin.	Ash.	Residual.
Plums	0·22	0·22	1·74	4·32	3·76	3·76
Pears	4·98	10·31	0·84	4·46	1·80	8·37
Apples	3·90	5·22	2·68	4·54	1·96	2·92

M. M. P. M.

Water in Seeds. By F. TSCHAPLOWITZ (*Landw. Versuchs-stat.*, xix, 412—419).—The smaller seeds of melons, gourds, corn, and peas absorb more water when soaked in that liquid than is taken up by the larger seeds; the total quantity absorbed is influenced by the length of time which elapses before the rootlet appears. More water is absorbed by those seeds which begin to germinate only after a considerable time, than by those which germinate quickly. M. M. P. M.

Specific Gravities of Seeds. By F. TSCHAPLOWITZ (*Landw. Versuchs-stat.*, xix, 420).—The author's method is shown by himself to yield unsatisfactory results. M. M. P. M.

Baltic Peat. By G. THOMS (*Landw. Versuchs-stat.*, xix, 423—434).—The detailed results of analyses and of physical properties of various peats are given in the original paper: there is nothing remarkable in the numbers. M. M. P. M.

Analytical Chemistry.

Portable Apparatus for Volumetric Analysis. By F. SESTINI (*Gazzetta chimica italiana*, vii, 225—226).—This apparatus combines the vessel for holding the standard solution with a burette, the former serving as a support for the latter. It consists of a tall cylindrical jar for holding the standard solution, closed with a cork: through this passes a safety-tube and also another vertical tube bent twice at right angles and communicating with the top of the burette; it reaches to the bottom of the jar. The burette is likewise closed with a caoutchouc stopper, through which, besides the bent tube passing to the bottom of the jar, there is another communicating with a Liebig's bulb. The burette is supported at the bottom near the tap by a metal arm attached to the cylindrical jar; this, together with the bent tube before mentioned, forms a stand for the burette. On applying suction to the Liebig's bulbs, the standard solution flows into the burette, whilst air enters the jar through the safety-tube. C. E. G.

Modification of Sauer's Method for Estimating Sulphur. By H. WEIDEL and M. VON SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 1131—1135).—The substance placed in a boat and covered with five or six times its weight of fused boric anhydride, is burnt in a current of oxygen, and the gases are passed over red-hot platinum sponge or platinised asbestos or pumice with which the fore part of the tube is filled; the boric acid serves to combine with the metal if the substance operated on is a salt, and the platinum causes the oxidation of the sulphurous acid to sulphuric anhydride. The escaping gases are passed through two Peligot's tubes filled with bromine-water, to oxidise the last trace of sulphurous acid, although this is scarcely necessary, and when the burning is completed, the sulphuric acid in solution is weighed as barium salt in the usual way. The analytical results obtained with seven sulphur-compounds, including salts of difficultly combustible sulphonic acids, are given, and they agree closely with theory. C. E. G.

On Thorpe's and Bunsen's Methods for the Estimation of Nitrogen in Nitrates. By S. W. JOHNSON (*Amer. Jour. Sci.* [3], xiii, 260).—The author made three trials of Thorpe's method (which consists in the reduction of the nitrate by slips of zinc coated with spongy copper); the first showed a deficiency of 45 per cent. of the total quantity of nitrogen, and in the second and third more acid was present in the receiver after the experiment than before, in consequence of the action of the evolved nitric oxide on the oxygen and water of the receiver. In a fourth experiment, made with a copper-zinc couple prepared according to Gladstone's directions, the deficiency of nitrogen was 8·64 per cent.

In Bunsen's method the reduction is effected, in presence of 250—300 c.c of water and excess of caustic potash, by zinc-iron couples prepared by twisting together slips of the two metals. The results showed a deficiency of 0·35 to 0·60 per cent. C. W. W.

Schönbein's Test for Nitrates. By F. H. STORER (*Chem. News*, xxxvi, 115).—This test consists in reducing the nitrate by nascent hydrogen evolved from zinc and sulphuric acid, and adding iodo-starch paste. The resulting nitrous acid is said to produce a blue colour. When zinc or cadmium is being dissolved in sulphuric acid, however, hydrogen peroxide is formed in small quantity, sufficient to give a blue colour with iodo-starch paste, for hydrogen peroxide is not destroyed by a short ebullition. It is also volatile to a slight extent with water vapour. It is better to boil the suspected liquid with zinc or cadmium, and then add iodo-zinc starch, than to place a stick of one or other of these metals in a solution to which the starch has been added. The delicacy of the reaction depends also on the amount of sulphuric acid added. W. R.

Some Methods for the Estimation of Sulphur in Iron. By J. HIBSCH (*Dingl. Polyt. Jour.*, ccxxv, 61—64).—The author has examined some iron for sulphur on the method of Koppmayer (*Dingl. polyt.*, 1873, ccx, 184), by which it is determined by standarized solution of iodine. He finds the results always too high; and the method not to be recommended, either for technical or for accurate analyses. For technical purposes he recommends Gintl's method (*Dingl. polyt.*, 1870, cxcvii, 168). In this the powdered iron is digested in chloride of iron, the residue is fused with potash and nitre, and the sulphur determined in the product. For exact analyses and scientific research, the author prefers the method of Fresenius (*Quant. Analysis*) with Weselsky's modifications, viz., the oxidation of the sulphide of lead with bromine. This shortens the time necessary for an analysis. For commercial purposes the author suggests a method which takes far less time and gives good results. He passes chlorine over the heated iron and collects the SCl_2 in U-tubes filled with hydrochloric acid and water. Sulphuric acid is formed ($SCl_2 + 4H_2O + HCl + 4Cl = H_2SO_4 + 7HCl$), and determined in the usual way.

Material.	Percentage of Sulphur.						
	Koppmayer.	Fresenius.	Gintl.	With chlorine.	Average.		
					Koppmayer.	Fresenius.	Gintl.
White pig	0·749 0·682	0·652 0·535	0·509	—	0·715	0·593	0·509
Grey pig.	0·127 0·121	0·102 0·098	— —	— —	0·124	0·100	—
White pig..	—	0·466	—	0·526	—	—	—

S.

Determination of Phosphorus in Pig Iron and Iron Ores. (*Dingl. polyt. J.*, ccxxv, 158—161).—Several methods or modifications of old methods are here given and compared.

Cairns (*Iron*, April, 1877) dissolves the ore in hydrochloric acid and potassium chlorate, evaporates to dryness and heats strongly; redissolves; precipitates with ammonia; dissolves the precipitate in nitric acid; obtains the molybdate precipitate; dissolves it; and precipitates the phosphate of magnesium and ammonium.

Stöckmann (*Zeit. für Anal. Chemie*, 1877, p. 174) finds that the results are low when the iron is dissolved in aqua regia. From the same specimens he got ·088 per cent. when he employed hydrochloric acid and ·057 with nitro-hydrochloric acid. He recommends treatment with nitric acid, and after evaporating to dryness, to dissolve in hydrochloric acid, and then to proceed as usual after this hydrochloric acid solution has been evaporated nearly to dryness.

C. Holthof (*Zeit. für Anal. Chemie*, 1877, p. 189) precipitates basic phosphate from an acetic acid solution. He finds the precipitation from this redissolved precipitate by ammonia and magnesium chloride in presence of citric acid to give very low results.

Korschelt (*Verhand. des Ver. zur Beförd. des Gewerbfleisses*, 1877, p, 267—277), in a prize essay, has tried to perfect the method of obtaining a precipitate at the first precipitation, which shall have a constant composition and not be decomposed at temperatures over 100° C. He uses a potassium-molybdate solution, obtained by adding 2 parts of molybdic acid to 2 of pure potash in 12 of water. After cooling, 1 part acetic acid, 4 of water, and $15HNO_3$ are added and filtered. 50 c.c. of iron solution are used and 30 c.c. of molybdate added at 30°. The precipitate can be dried at 120° The author gives 1·727 per cent. as percentage of phosphorus in the precipitate. Rammelsberg, who recommends the method, gives 1·768 as the percentage of phosphorus.

S.

On Stolba's Method for the Alkalimetric Estimation of Phosphoric Acid. By F. Mohr (*Zeitschr. Anal. Chem.*, xvi, 326—328).—In *Zeitschr. Anal. Chem.*, xvi, 100, Stolba gives a method of determining ammonio-magnesic orthophosphate alkalimetrically instead of by igniting and weighing. It is supposed that under all circumstances the phosphoric acid is separated in the form of the above-named salt, and that tincture of cochineal is used as indicator. The following additional observations are made by the author in regard to Stolba's accounts. The double salt mentioned consists of $P_2O_5.2MgO.(NH_4)_2O$ if imagined in the anhydrous state; it contains 1 atom of phosphoric acid and 3 atoms of real base. By saturating 2 atoms of base with acid, phosphoric acid with 1 atom of base is left in the neutral state, and the smallest excess of acid occasions the acid reaction. The double salt, known as "microcosmic salt," consists of $P_2O_5.Na_2O.(NH_4)_2O + 9aq$, reacts alkaline, and may also be measured alkalimetrically. 1 gram required 4·8 c.c. of normal hydrochloric acid. It contains, according to the formula, $\frac{71·36}{209·36} = 0·3408$ gram phosphoric acid; therefore 1 c.c. normal acid $= \frac{0·3408}{4·8} = 0·071$ gram P_2O_5, *i.e.*, almost exactly $\frac{1}{1000}$ of the atomic weight of phosphoric acid. By precipitating 1 gram of microcosmic salt with the magnesia mixture and titrating the washed precipitate, according to Stolba, 9 c.c. of normal acid, *i.e.*, twice the above quantity was used. This is easily explained by the fact that the sodium salt contains 1 atom of basic water, which is alkalimetrically inactive, while the magnesium salt really contains 3 atoms of base. In the first case 1 atom of base and in the second 2 atoms are saturated. By heating the sodium salt in a platinum capsule till it melts to a glass, $P_2O_5.Na_2O$ is left, which, when dissolved in water, is perfectly neutral. If, however, the ordinary sodic phosphate with 2 atoms of soda and 1 atom of basic water be measured alkalimetrically, it requires before and after ignition the same quantity of acid, because the atom of basic water remains inactive and the two atoms of soda are still present.

An empirical phosphoric acid solution, which contains 10 grams phosphoric acid in 1 litre, is best prepared from microcosmic salt by dissolving 29·324 grams of the latter in a litre of water. In order to prepare an equally strong solution of hydrochloric acid, 20 c.c. of pure hydrochloric acid of ordinary strength are made up to 1 litre with distilled water. 10 or 20 c.c. of the titrated phosphoric acid solution are poured into a porcelain dish and treated with tincture of cochineal, which is at once turned violet. Hydrochloric acid is then run in from a burette divided into $\frac{1}{10}$ c.c. till the last drop converts the violet colour into the yellow. It is very important to exclude the smallest traces of ferric oxide, which greatly interferes with the results of the reaction. Free phosphoric acid cannot be titrated by this method, as the former is generally accompanied by other acids. It is therefore more advisable to precipitate the acid with ammonia and magnesia mixture, and to measure it with hydrochloric acid, in which case all the other acids are separated from the phosphoric acid.

D. B.

Valuation of Cements. By W. MICHAELIS (*Dingl. polyt. J.*, ccxxiv, 188—193, 287—292, and 417—424).—The general results of the investigations of a commission appointed to enquire into the subject of valuation of cements were as follows:—

1. Portland cement should invariably be sold by one and the same system of weights and measures.

2. Slow-setting Portland cement is to be preferred for most purposes to that which sets quickly. Slow-setting cements are those which do not solidify before a minimum time of half an hour.

3. A cake of good cement, when placed under water for some time, should show no cracks, nor exhibit any tendency to crumble.

4. Portland cement should be ground so fine that when passed through a sieve of 900 meshes to the square centimeter, not more than 25 per cent. remains on the sieve.

5. The binding power of a cement should be determined by a test made with sand. The experiment should always be carried out under the same conditions and in the same apparatus. The apparatus and test materials of Frühling, Michaelis, and Co., of Berlin, are recommended.

6. One part of Portland cement with three parts of sharp sand, after one day in air and 27 days in water, should bear a minimum weight of 8 kilos. per centimeter. The sand used must not vary in quality or in fineness. For details the original paper must be consulted.

M. M. P. M.

On Ammonium Vanadate precipitated from Alkaline Vanadates with Ammonium Chloride. By B. W. GERLAND (*Chem. News*, xxxvi, 29).—It is found that, under all circumstances, ammonium vanadate cannot be precipitated free from potassium by ammonium chloride if potassium salts are present in solution, but that the purity of the precipitate is not affected by the presence of sodium.

Ammonia behaves somewhat like potash; the sulphates of vanadium also retain potassium. E. W. P.

Estimation of Chromium and Aluminium in Steel and Iron. By A. A. BLAIR (*Amer. Journ. Sci.*, xiii, 421).—Five grams of borings are placed in a half-litre flask with 20 c.c. of hydrochloric acid diluted with 3 or 4 times its volume of water, and the flask is closed with a valved stopper. If necessary, heat is applied, and when the iron is dissolved, the valved stopper is replaced by a solid one, and the flask cooled. The flask is then about three-fourths filled with water, and a slight excess of barium carbonate (free from sulphate) added gradually. The flask should be thoroughly shaken several times, loosening the stopper occasionally to allow the carbonic acid to escape, and left over-night. The liquid is then quickly filtered; the precipitate washed with cold water and dissolved in hydrochloric acid; the solution diluted; the sesquioxides of iron and chromium precipitated with ammonia; and the excess of ammonia expelled by boiling. The precipitate is washed, dried, and fused with 3 grams of sodium carbonate and 0·5 gram of nitre, the heat being continued till all the nitre is decomposed. The fused mass is dissolved in water, and the solution filtered from the ferric oxide is evaporated with hydrochloric acid and alcohol. The chromic oxide is dissolved in hydrochloric acid, filtered from silica, and precipitated by ammonia in the usual way. The chromic oxide is calculated to chromium by the factor 0·6853.

For the determination of aluminium in steel, the first part of the process is the same as for chromium, as far as the washing of the precipitate obtained with barium carbonate, which in this case is dissolved in hydrochloric acid, and the barium precipitated with sulphuric acid; the barium sulphate is removed and the excess of acid expelled by evaporation. The ferric oxide (and alumina and chromic oxide) are separated by ammonia, ammonium sulphide, and citric acid. The chromium (if any) is converted into alkaline chromate by fusion with sodium carbonate and nitre; the mass is dissolved in water; and without filtering, potassium chlorate and hydrochloric acid are added, and the solution is evaporated to dryness in the water-bath, keeping the chlorate in excess. Redissolve in water; add a slight excess of ammonium carbonate and boil off all smell of the latter; filter; wash with hot water; add to the solution an excess of hydrochloric acid, and, after the greater part of the chlorate is decomposed, add a little alcohol and precipitate the chromium as before. The alumina obtained by precipitation with ammonium carbonate is apt to be contaminated by silica and lime (from the citric acid), from which it can be separated by dissolving in hydrochloric acid, evaporating to remove silica, redissolving in hydrochloric acid, and precipitating with ammonium carbonate, care being taken to remove all excess of carbonate by boiling.

C. W. W.

Volumetric Estimation of Tin. By H. PELLET and A. ALLART (*Bull. Soc. Chim.*, xxvii, 438—440).—The liquid must be free from iron, copper, antimony, and nitric acid. The tin is reduced to dichloride by adding to the boiling liquid hydrochloric acid in excess and a large proportion of zinc. After complete solution of the zinc, any tin that may have been precipitated will be redissolved if the ebullition be continued. The tin is estimated by the quantity of a standardised solution of ferric chloride or of cupric chloride, which must be added to the still boiling liquid till a light brown colour is produced.

R. R.

Detection of traces of Copper. By L. CRESTI (*Gazzetta chimica italiana*, vii, 220—222).—On immersing a small couple formed of zinc and platinum wires in a solution containing even a trace of copper, the latter is deposited on the platinum wire in the metallic state, and if this be exposed to the vapour of hydrobromic acid, it is converted into copper bromide. If, however, the platinum wire coated with copper be exposed whilst still moist first to the vapours of bromine, and then to those of hydrobromic acid, or *vice versâ*, an intense violet coloration is produced, even with a very minute quantity of copper. The best method of performing the experiment is to expose the moist film of copper to the mixed vapours of bromine and hydrobromic acid given off on treating potassium bromide with concentrated sulphuric acid. The tint may be conveniently observed by touching a white porcelain plate with the point of the moist platinum wire after exposure; after the experiment, the wire may be inserted into the flame of a Bunsen burner to show the green copper flame. The author considers the blue coloration to be due to a combination of hydrated copper bromide with hydrobromic acid. C. E. G.

Estimation of Zinc and Lead in Minerals by Electrolysis. By G. PARODI and A. MASCAZZINI (*Gazzetta chimica italiana*, vii, 222—224).—The authors find that zinc can be precipitated on platinum in a coherent film, which can be readily washed and weighed if the solution be first rendered ammoniacal and then acidulated with an organic acid, preferably acetic, and submitted to electrolysis, care being taken to adjust the current to the strength of the solution. The iron, lead, &c., present in calamine, blende, and other zinc minerals, should be removed by Schwartz's process previous to electrolysis. The presence of a minute quantity of lead greatly increases the coherence of the zinc film, if no mineral acid except sulphuric be present. Lead may be precipitated in a coherent state and of a dull colour by operating on solutions, preferably alkaline, containing phosphoric and tartaric acids. The presence of acetic acid tends to keep the positive pole free from lead peroxide. The authors intend soon to give the details of the process for the estimation of lead by this method.

C. E. G.

Determination of Manganese by Precipitation as Oxalate. By A. CLASSEN (*Zeitschr. Anal. Chem.*, xvi, 315—317).—According to Gibbs, a neutral and concentrated solution of a salt of manganese, when treated with a concentrated solution of oxalic acid and an excess of strong alcohol, is precipitated in the form of oxalate of manganese. This precipitate is very finely divided and is not suitable for quantitative work. It was therefore proposed to determine the amount of oxalic acid present in the precipitate by titration, but Fresenius and Leison found that this method was not accurate enough, as the separation of manganese oxalate was not complete even when a very large excess of alcohol was used. The author's experiments proved that by adding a concentrated solution of potassium oxalate (1 : 6) to a salt of manganese, and treating the mixture with strong alcohol, a filtrate was obtained perfectly free from manganese. The precipitate always however contains large quantities of the precipitant, which cannot be removed by washing. When acetic acid is used instead of alcohol a precipitate is formed which is very crystalline and easy to wash. Concentrated solutions may be filtered directly after precipitation; with dilute solutions it is advisable to wait a few hours. A mixture of alcohol and acetic acid answers the same purpose. In order to convert the oxalate of manganese into manganoso-manganic oxide, the precipitate is heated gently on the filter in a covered platinum crucible and then strongly in the air until constant in weight. The precipitation as oxalate of manganese with alcohol also takes place in a hydrochloric acid solution. The oxalates of nickel and cobalt react in like manner with concentrated acitic acid.

D. B.

Separation of Manganese from Lime. By A CLASSEN (*Zeitschr. Anal. Chem.*, xvi, 318—319).—In order to separate small quantities of manganous oxide from large quantities of lime, Rose recommends that the liquid be mixed with a sufficient amount of ammonium chloride to prevent precipitation by ammonia, and that the lime be precipitated as oxalate and the manganese in the filtrate by ammonium sulphide. Since it is impossible to prevent small quantities of manganese being carried down with the calcium oxalate, the author acidifies the solution after treatment with ammonia with acetic acid. Under these circumstances, however, the precipitate could often not be obtained free from manganese. In conclusion, it is stated that, although the separation of manganese oxalate in presence of a sufficient quantity of hydrochloric acid is prevented by means of alcohol, while calcium oxalate is precipitated, it was thought that probably the precipitation of manganese in presence of lime would be avoided. A large number of experiments undertaken in this direction gave negative results, the calcium oxalate being contaminated with manganese, no matter whether calcium or manganese predominated.

D. B.

Separation of Manganese from Iron. By KRÄMER (*Zeitschr. Anal. Chem.*, xvi, 334).—Stöckmann (*ibid.*, xvi, 172) has given an account of the estimation of manganese in spiegeleisen, in which he mentions that, when iron is separated from manganese with acetate of sodium, only 1 per cent. of manganese is left in the iron precipitate. The author, however, states that the amount of manganese retained in the precipitate depends entirely upon the washing of the latter. After washing the precipitate with hot water till the nitrate of siver fails to form a precipitate in the filtrate, the quantity of manganese present in the ferric oxide precipitate does not exceed more than 0·1 per cent. Care must be taken not to omit the addition of one or two drops of dilute acetic acid; otherwise the separation of iron from manganese, after previously neutralising with carbonate of soda, will not be quite successful. D. B.

Quantitative Separation of Iron and Manganese in Ferromanganese Ores. By A. FIMARO (*Gazzetta chimica italiana*, vii, 286—294).—2 or 5 grams of the finely powdered mineral are dissolved in hydrochloric acid, and the solution evaporated to dryness after adding a drop or two of nitric acid to peroxidize the iron. The residue is heated with a small quantity of hydrochloric acid, diluted, and filtered from the separated silica, which is ignited and weighed. The solution containing the iron and manganese is exactly neutralised with ammonia, and precipitated with a slightly acid solution of ammonium benzoate or succinate; and the precipitate, which contains the iron and alumina, is collected, washed first with water, then with dilute ammonia, and finally dried, ignited, and weighed. The iron and alumina in this precipitate may then be separated and determined in the usual manner. The manganese is precipitated as sulphide by sulphide of ammonium, and determined as manganoso-manganic oxide in the usual way. If the mineral contains copper or zinc, these must be removed by passing sulphuretted hydrogen through an acetic solution, previously to the precipitation of the iron. The magnesia and lime are determined in the filtrate from the manganese sulphide. The author considers this process to be especially valuable when the manganese is not in very minute quantity, and preferable to the separation by means of—1. Ammonia and ammonium chloride. 2. Barium or calcium carbonate. 3. Sodium acetate and chlorine or bromine, or hypochlorite. 4. Lead oxide. 5. Conversion into sulphates, all of which he has tried. Critical remarks on these processes are given.

C. E. G.

Apparatus for Estimating Marsh-gas in Mines. By J. COQUILLION (*Compt. rend.*, lxxxiv, 458—459).—The blue aureola which surrounds the flame of the safety lamp when in an explosive atmosphere, is at present the only means used for ascertaining the presence of fire-damp in mines, and from 6 to 8 per cent. of marsh-gas is necessary to produce this effect. In order to detect a much smaller quantity of gas, the author has devised two pieces of apparatus, one for use in the mine itself, the other to be used above ground as a check upon the first, and to estimate the gas collected at different parts of the mine. The principle depends upon the fact that hydrogen and hydrocarbons generally are completely burned in presence of oxygen, without detonation, by means of a palladium wire brought to a white heat. The carbonic anhydride thus produced is afterwards estimated in a graduated tube, and the percentage of carbon present ascertained. No further description of the apparatus is given, neither is its working more fully explained.

J. W.

Estimation of the Gases dissolved in Water. By J. W. THOMAS (*Chem. News*, xxxvi, 37).—An addition to the ordinary apparatus employed for the estimation of gases dissolved in water is recommended. This consists in introducing between the flask containing the water and the Sprengel pump, a bottle, whereby any water carried over from the flask is prevented from entering the pump. This bottle should first be exhausted before heating the water, and may itself be afterwards heated, so as to drive off any gases that might be dissolved in the water which it contains.

E. W. P.

Determination of the Organic Matter in Potable Waters. By W. DITTMAR and H. ROBINSON (*Chem. News*, xxxvi, 26—29).—The object in view was to obviate the great expenditure of time which is necessary for the correct working of Frankland's method. The water is boiled down in a slanting glass flask with sulphurous acid, finally evaporating on the water-bath; the residue thus obtained is burnt with copper oxide (which is preferred, because it is impossible to free lead chromate from carbonate), and the carbon determined. It was found that india-rubber tubing furnished enough carburetted hydrogen to air passed through it, to yield when burnt a precipitate with baryta-water.

The organic nitrogen is determined by boiling down half a litre of the water in a flask connected with a condenser, and "Nesslerising" the free ammonia which passes over. When 19-20ths of the water has been got rid of, ferric chloride and sulphurous acid are added; the residue obtained is then placed in a copper or silver boat, and moistened with a drop of water; 3 grams of a fused mixture of equal parts of pure baryta and sodium soda are added; the whole is then burnt in a current of hydrogen; and the amount of ammonia determined by Wanklyn's colorimetric method. The time required for the nitrogen determination is about four hours. For details of precautions, and for analyses, the reader is referred to the original paper.

E. W. P.

Chromic Acid a Test for Malic Acid. By G. PAPASOGLI and A. POLI (*Gazzetta chimica italiana*, vii, 294—296).—As a solution containing malic acid, when boiled with a few drops of sulphuric acid and some potassium dichromate, gives an odour resembling that of ripe fruit, the author utilises this reaction for a preliminary examination of the precipitate obtained by calcium chloride in alcoholic solution, which may contain citric, succinic, and malic acids. The precipitate, after being entirely freed from alcohol, is decomposed with dilute sulphuric acid, and the filtered liquid boiled with a small quantity of potassium dichromate. If the liquid remains yellow, succinic acid alone is present, and may be recognised by ferric chloride in the usual way; if the liquid turns green without giving any odour, it indicates the presence of citric, or of citric and succinic acids, which may be tested for as usual; but if the liquid turns green and an odour of ripe fruit is developed, it indicates the presence of malic acid, and it then becomes necessary to examine the precipitate for all three acids systematically.

C. E. G.

Some Methods of Estimating Tannins. By H. R. PROCTER (*Chem. News*, xxxvi, 58).—The author commences by giving an account of the various processes for estimating tannins. He objects to the process in which the specific gravity of the tannin solution is taken before and after forcing it through a piece of raw hide, on account of the absorption of free acids by the hide. Volumetric valuation by means of a solution of gelatin and alum is useful only as a rough estimate. In fact the great difficulty lies in the fact that all tannins do not form the same proportion by weight of any compound suitable for weighing. This objection applies especially to Fleck's process of precipitation by cupric acetate in presence of ammonia to dissolve gallic acid and colouring matter. . The mean error of this process, the results being obtained by drying the copper precipitate in an air-bath at 100°, is ± 4·2 per cent.

Mr. H. Allen's volumetric process with lead acetate, using as indicator a mixture of ammonia and potassium ferricyanide, is open to objection on the score of equal precipitation of gallic acid; moreover, the end reaction is indistinct unless each drop be filtered before mixing it with the indicator.

Mittenzwey's process, improved by Terreil, of estimating the amount of oxygen absorbed by an alkaline solution of the tannin, is difficult and tedious, though probably accurate.

The author gives the preference to Löwenthal's method, described in this *Journal* (1877, i, 745), over all the methods which have been described, and also over Carpeni's process of precipitation with ammonio-acetate of zinc, Jean's oxidation process with iodine in presence of sodium carbonate, and Pouchet's method of oxidising with potassium permanganate in presence of caustic potash. W. R.

New Reaction of Morphine. By G. PELLAGRI (*Gazzetta chimica italiana*, vii, 297—298).—The suspected substance, evaporated at a gentle heat if necessary, is dissolved in concentrated hydrochloric acid, a small quantity of sulphuric acid is added, and the mixture evaporated on an oil-bath at a temperature of 100° to 120°. If morphine be present, the liquid acquires at its edges a purple colour, which is not masked by the carbonisation of organic matter, and when all the hydrochloric acid has been driven off, the sulphuric acid remains of a red colour. This dissolves in concentrated hydrochloric acid, and becomes violet on neutralisation with sodium bicarbonate. This colour is insoluble in ether, but if a few drops of hydriodic acid be added, it changes to green, and is now soluble in ether, colouring it purple. These colour changes are very delicate, and are common to apomorphine, into which the morphine is changed by the action of the acid. Codeine also gives the same reactions, but its solubility in ether serves to distinguish it from morphine. Brucine when treated in a similar manner gives a blue colour on neutralisation with sodium bicarbonate, but the reaction is not delicate. C. E. G.

Spectroscopic Estimation of the Amount of Hæmoglobin in Human Blood. By MAX WISKEMANN (*Zeitschr. für Biologie*, xii, 434—447).—The author, employing Vierordt's method of quantitative spectrum analysis, has examined the blood in man in physiological and pathological states. The greatest errors in the estimation by this method of the amount of hæmoglobin in the blood in 100 parts do not, according to the author, amount to more than 0·2. In a table containing numerous estimations, the author gives in each case the coefficient of extinction found for the second absorption-band of the oxyhæmoglobin (on dilution 100 times, and through a layer one centimeter in thickness), which forms a directly comparable value of the amount of hæmoglobin in a unit by volume of blood. For healthy women from 20 to 30 years old, he finds this coefficient to be on average 0·965. In newly born children a considerable increase in the quantity of hæmoglobin was observed; there was, however, no essential difference between blood from the skin of the nates and that from the umbilical artery, neither was there any noticeable diminution in the amount of hæmoglobin during the first week after birth. The pathological cases the author divides into two classes, first, those in which the blood suffered pre-eminently; and, secondly, those in which the blood either suffered equally with the rest of the body, or was scarcely at all affected. To the second class belongs a case of phthisis, with much emaciation, examined three hours before death, in which the blood showed comparatively a very slight diminution in hæmoglobin. In the former group occurs a case of asthenic pneumonia.

The patient, who was previously always healthy, lost within eight days half her blood-corpuscles without the appearance of any hæmorrhage. Eight days later the content of hæmoglobin had increased considerably. In a case of ovarian tumour and ascites, in spite of considerable loss of albumin, the loss of hæmoglobin, if any, was very slight. E. C. B.

Characters of the Normal Constituents of Beer, as tested by the Methods of Stas-Otto and Dragendorff. By R. S. TJADEN MODDERMANN (*Zeitschr. Anal. Chem.*, xvi, 328—332).—By a note in *Zeitschr. Anal. Chem.*, xvi, 116, on the presence of a substance in beer which is similar to colchicine, the author was led to give an account of the following investigations. In 1876 a sample of imperial stout from Bass and Co.'s brewery was analysed. After removal of the carbonic acid by shaking up the beer moderately, the specific gravity was tried at 15°, and gave 1·029. The alcohol was estimated in weight per cent. by distillation after neutralising with lime-water. Quantity obtained 5·9 p.c. The specific gravity of the extract was 1·049, corresponding, according to Balling, with 9·901 p.c. of solid constituents. The ash was equal to 0·396 p.c. The beer was tested according to Dragendorff's methods I and II (*die gerichtlich-chemische Ermittelung von Giften*, second edition, p. 300), also according to the Stas-Otto method for alkaloïds and foreign bitter principles. According to Dragendorff's method (II), the bitter of the hop and certain bitter substances contained in the fermented malt-extract are removed by warming the beer, in order to expel the carbonic acid, and treating it with acetate of lead after cooling. The filtrate is freed from lead by means of sulphuric acid, or, better, by sulphuretted hydrogen, and the liquid evaporated to one-fourth or one-fifth of its bulk. Petroleum-ether, benzene, &c., did not leave a residue when shaken up with the liquid and evaporated. According to Dragendorff's method (I) and Stas-Otto's method, petroleum-ether, benzene, chloroform, and ether gave, from an acid as well as an alkaline solution, yellow to reddish-brown residues. The similarity of these residues to colchicine is, however, according to the author's experience, a matter of much less consideration. It is limited to the bitter taste, the partial solubility in water with a pale yellow colour, which is intensified by potash, and, lastly, the precipitability by chlorine-water. But these conditions do not even correspond with colchicine. An aqueous solution of the latter assumes a darker yellow colour, not only with potash, but also with mineral acids. Such, however, is not the case with the above yellow residues of beer. Precipitates with tannin and solution of iodine (indicating the presence of alkaloïds) could not be obtained. The coloration with nitric acid, which is said to be obtained from beer-residues, has never been observed by the author.

The following are the properties of beer-residues which, according to the Dragendorff and Stas-Otto methods, are extracted from an acid or alkaline solution by petroleum-ether, benzene, chloroform, and ether:—Colour: pale yellow to reddish-brown. Form: amorphous. Taste: bitter in slightly alcoholic solution. Solubility:

partly soluble in water, with pale yellow colour, leaving a residue consisting of a deep yellow to reddish-brown resinous substance, totally soluble in alcohol, ether, petroleum-ether, benzene, and chloroform. Smell: slight smell of caramel. The solutions do not reduce Fehling's liquid, not even after warming with dilute sulphuric acid. By heating with soda-lime a scarcely conceivable trace of ammonia is evolved. The residues are, therefore, almost free from nitrogen.

Aqueous Solution.—Potash: deep yellow colour, not altered by warming; after neutralising it turns pale yellow. Chlorine and bromine water: white turbidity, soluble in ammonia, with pale yellow or reddish-brown colour. The intensity of the colour alters accordingly with the quantity of chlorine or bromine water added. Normal and basic acetate of lead: slight precipitate. Iodopotassic iodide, tannin, chloride of gold: no change. Ammoniacal silver solution is not reduced. Chloride of gold treated with potash is reduced.

Aqueous Solution evaporated.—(Yellowish-brown residue). Nitric acid (sp. gr. 1·37) does not alter the yellowish-brown colour of the residue. English sulphuric acid gives a dark brown colour. Nitric acid does not alter this colour; chlorine water destroys it.

Alcoholic solution of cupric acetate gives a bluish-green precipitate.

Lead acetate gives a colourless precipitate, and iodopotassic iodide, tannin, and gold chloride give no precipitates. The residues from hops behave in a similar manner, but the colour is a paler yellow. By prolonged digestion with ether, residues are obtained which are no longer perfectly amorphous, but exhibit under the microscope the appearance of long needles.

In conclusion, the author mentions that although the above results are very incomplete, they nevertheless show how the presence of these unavoidable constituents of beer hinders the reactions for certain adulterations. For instance, the yellow colour with potash is no proof of the presence of bitter principles from Gentiana or Daphne Mezereon. In certain cases it may perhaps be more advantageous to dissolve the residue in alcohol and to precipitate the hop resin, which may prevent admixtures from crystallising by means of acetate of copper.

D. B.

Technical Chemistry.

On the Contamination of Air arising from Artificial Illumination, and on the Distribution of Carbonic Anhydride in Close Rooms. By Friedrich Erismann (*Zeitschr. für Biologie*, xii, 315—365).—This investigation is a continuation of one somewhat similar, on the deterioration of air by sewer gases. A comparison is made of the various materials used for lighting dwelling-houses. The injurious effect cannot be calculated from the absolute amount of carbonic anhydride present: for a considerable quantity of the illuminating substance always escapes unburned, and this amount bears no constant relation to the carbonic anhydride, and varies with the temperature and source of the flame. Special attention had also to be given to the ventilation of the room in which the experiments were carried out; yet, in spite of all possible care, the rate of ingress and egress of air could not be kept constant. The probability is also that the amount of contamination of air, although it had to be reduced to a normal quantity of light, bears no proportion to the illuminating power of the burning material: for one flame giving twice as much light as another does so partly in consequence of more perfect combustion.

The manner of conducting the research was as follows:—The air was drawn by means of an aspirator through a tube which split into two separate tubes. One of these tubes was connected with other tubes filled with baryta; the other communicated with a red-hot tube containing copper oxide: and the carbonic anhydride produced by the combustion of the organic matter contained in the air, as well as that present in the air before combustion, was collected in tubes filled with baryta. All the excess of carbon not existing in the air as carbonic anhydride was presumed, for the sake of simple comparison, to have been CH_4. The room in which the experiments were carried out contained about 10 cubic meters, and was perfectly free from draught except when a strong west wind was blowing. The temperature of the air, before and after each experiment, which lasted eight hours, was observed. The amount of air passing through the aspirators varied from 15 to 18 litres. The temperature varied from 16° to 22°. The illuminating materials compared were stearin candles, petroleum, vegetable oil, and gas. After ascertaining the normal amount of carbonic anhydride and oxidisable carbon compounds in the air, the amount formed by the combustion of the abovementioned substances was determined, and the quantity of CO_2 and CH_4 previously existing in the air deducted; the result is the amount of carbonic anhydride and imperfectly burned organic matter arising from the source of light under experiment.

Without entering into the details of the experiments, the following general conclusions may be drawn:—1. In every case of artificial illumination, the air of a close room contains more carbonic anhydride and organic matter than when no light is present. 2. The proportion of CH_4 to CO_2 varies, not only with the nature of the burning material, but also in different strata of the air of the room, when the same material is employed. No constant relation can be found between them. 3. The air should never contain more than 0·6 or at most 0·7 per thousand of carbonic anhydride, otherwise products of imperfect combustion are present in large quantity. A smaller amount of carbonic anhydride, however, gives no proof of the freedom of the air from such products. 4. The position of the stratum of air in which most products of combustion are found, depends on the nature of the burning material. When candles are employed, the higher strata are more impure than the lower; but generally by far the largest portion of carbonic anhydride produced by combustion is removed from the room by natural ventilation. 5. Petroleum, when burned in well constructed lamps, gives rise to less carbonic anhydride, and, what is more important, to less imperfectly burned matter, than any other illuminating agent. For equal light, stearin candles render the air most impure. Generally the proportion of imperfectly burned products is nearly 1 : 4 : 4 : 7, for petroleum, gas, oil, and candles.

An ordinary room, the contents of which amount to 100 cubic meters, would contain about the following amount of carbonic anhydride and other substances containing carbon (the latter calculated as marsh-gas) for a light equal to six candles:—

	CO_2.	CH_4.
When lighted with petroleum	56 c.c.	1·7 c.c.
„ „ gas	47 „	6·9 „
„ „ oil	109 „	7·2 „
„ „ candles	125 „	18·7 „

It is hardly possible that so small an amount of gas could have any injurious action on the organism, especially when gas or petroleum is used, and the rooms are ventilated in the usual manner. Indeed, although four men evolve as much carbonic anhydride and other products of respiration as six candles, yet the ventilation through chinks in the door, &c., carries off so much, that instead of 57·6 per thousand of carbonic anhydride, which would be the actual proportion in an unventilated room, only 1·99 per thousand was found. As this experiment was carried out in a small room of 10 cubic meters contents, and as some school-rooms have been found to contain 5 or 6 per thousand of carbonic anhydride, it is clear that the ventilation of such rooms must have been lamentably deficient.

The temperature at the floor during the experiments rose by 2—3°; at the roof the increase was much more marked, about 10°. But the following rule remained pretty constant; for equal amounts of light oil and gas raise the temperature much more than petroleum; candles give out least heat.

For illuminating power equal to six candles, petroleum costs, in 24 hours, 2½*d.*; gas, 6½*d.*; rape-oil, 7½*d.*; and candles three shillings. These numbers are calculated from the current prices at Munich. Paraffin lamps with round wick give out more light in proportion to the oil burned, if the air-holes below are partially closed; by making the opening half the usual size, this effects a saving of about one-third of the oil.

The remainder of this paper is occupied with an investigation of the position of carbonic acid in the air-strata of a room. When the temperature of the gas is the same as, or lower than that of the air, it remains chiefly in the lower layers; but, if higher, the gas ascends and mixes with the air. W. R.

On Putrescent Organic Matter in Potable Water. By G. Bischof (*Chem. News*, xxxvi, 2—3).—A number of observations point to the conclusion that those low forms of organic life, which in all probability form the specific poison of cholera, typhoid fever, and other diseases, by gaining admission to drinking water polluted by putrescent matter, are the causes of derangements of the human system, and that these organisms or their germs are not infectious as long as surrounded by fresh organic matter, but show their poisonous virulence as soon as fermentation sets in. As chemical analysis is incapable of discriminating between living or dead, fresh or putrescent organic matters, and as it is difficult to decide with a microscope the existence or non-existence of putrefaction bacteria or their germs in water, the author devised an indirect method based on the fact that the presence or absence of putrefactive agencies in water may be determined by their action upon organic matter. The test which he selected is fresh meat, as the slightest putrescent changes in it can most readily be detected by its smell. The experiments, which were originally made with a view of determining the improvement of water by certain filtering media, were carried out in the following manner:—Some fresh meat is placed on the perforated bottom of a stoneware vessel, which is filled two-thirds with the materials to be experimented upon, and, lastly, with water. At the upper part of the vessel an inverted U-tube is fixed, which prevents any bacteria or their germs from passing through the outlet tube into the bottom of the vessel. A tube which is sealed at the bottom passes down through the material experimented upon, to allow of the temperature being measured in close proximity to the meat. The apparatus thus prepared is immersed in a boiler filled with cold water, which is gradually heated and kept boiling for several hours. The object of this is to destroy any germs adhering to the meat. The temperature at the bottom of the sealed glass tube during the boiling in each of the following experiments was 93·95°. After cooling, the Chelsea Company's water was constantly passed through the vessel. It is thus evident that any putrefaction bacteria or their germs in the water would after a time render the meat putrid, or, if it remained fresh, they must have been absent, or at least inactive, when the water reached the meat.

Experiment I.—The vessel was filled with spongy (metallic) iron and treated as before described; after a fortnight the meat was perfectly fresh.

Experiment II.—The vessel filled with animal charcoal; after a fortnight the meat showed strong evidence of incipient putrefaction.

Experiment III.—Water continuously passed through a vessel filled with spongy iron for four weeks; even then the meat was perfectly fresh and hard.

Experiment IV was a repetition of II, the filtration being continued for four weeks. The meat was soft and quite putrid.

Experiment V.—In order to determine whether (in I and III) bacteria were merely mechanically retained, the vessel was charged with spongy iron from which all the finer particles had been separated by a sieve with thirty holes on the linear inch. After four weeks the meat was perfectly fresh.

Experiment VI.—In the former experiment the meat was in contact with water from which the iron in solution had not been separated. With the view of ascertaining whether the iron in solution was the preserving agent, a stoneware vessel was charged underneath the spongy iron with pyrolusite and sand, so as to abstract the iron from the water before it came in contact with the meat. After four weeks' filtration the meat was found perfectly fresh.

Experiment VII.—By a separate experiment the author ascertained that oxygen is completely abstracted from the water during its passage through spongy iron. In order to determine whether the absence of oxygen be the cause of the preservation of the meat, an evaporating basin was inverted over the meat. This must have retained a quantity of air in its cavity, the air being gradually dissolved by the water in close proximity to the meat. After four weeks' filtration the meat was perfectly fresh, and the small quantity of gas still in the cavity of the basin was perfectly free from oxygen.

Experiment VIII.—Fresh meat was placed at the bottom of a glass vessel and left standing, covered with about four inches of spongy iron and water. The water in this instance was not boiled. After three weeks the meat was very bad, showing that the action of the putrefaction bacteria adhering to the meat was not prevented by the spongy iron above; and if during the previous experiments with spongy iron, agencies capable of causing putrefaction had at any time come in contact with the meat, the latter must, as in this last experiment, have shown marks of their action. It therefore appears that bacteria are permanently rendered harmless when passing into water through spongy iron. This conclusion is further corroborated by the observation that even effluent sewage-water, after passing through the spongy material, has remained perfectly bright for now five years, when exposed to light in a half-filled stoppered bottle.

The author believes that the action of spongy iron on organic matter largely consists in a reduction of ferric hydrate by organic impurities in the water. It is, morever, quite certain that a reducing action also takes place when ordinary water is passed through spongy iron; this is clearly indicated by the reduction of nitrates. The ferrous hydrate resulting from the reduction by organic matter may be reoxidised by the oxygen dissolved in the water, and thus the two reactions repeat themselves. This may explain why the action of spongy iron continues so long.

In conclusion, the author states that our knowledge of those low organisms which are said to be the cause of certain epidemics, is as yet too limited to allow of direct experiments upon them. Should those specific contagia not be destroyed when passing in water through spongy iron, then the separation of bacteria by spongy iron may afford means of isolating those germs of disease. Should it be favourable, then we shall have found in spongy iron the material to prevent the spreading of epidemics by potable water. D. B.

Composition of Boiler Incrustations. By E. FRANCIS (*Chem. News*, xxxvi, 15).—Sample I was a brown cake, half an inch thick, from a small egg-end boiler, using the water drawn from the southwest face of the anticlinal of Birmington in the middle coal measures. The incrustation was hard, only partially soluble in hydrochloric acid, and almost completely soluble in aqua regia.

Sample II was a very light grey cake, about three-eighths of an inch thick, obtained from a boiler fed by water from the Sheffield Water Company's mains. It was not entirely soluble in hydrochloric acid. Its analysis, as given below, shows that the water used was permanently hard, having little action upon the iron of the boiler.

Sample III formed an extremely hard residue, three-eighths of an inch thick, taken from a tubular boiler at Heeley near Sheffield, the water used being pumped from a well. It was difficult to powder, entirely soluble in aqua regia, and showed in places minute specks of metallic iron. The following are the complete analyses of the samples :—

	$CaSO_4$.	SiO_2.	$CaCO_3$.	Fe_2O_3.	MnO_2.	Al_2O_3.	P_2O_5.	Org matter and water.	Na and K.	CO_2.	Fe (metallic).		
I.	75·65	5·64	—	4·71	4·85	—	trace	8·61	trace	—	—	=	99·46 p.c.
II.	79·56	—	5·05	1·53	5·34	1·02	absent	7·75	trace	—	—	=	100·25 ,,
III.	37·06	—	—	38·98	10·36	1·62	—	8·80	trace	2·58	trace	=	99·4 ,,

D. B.

Regulation of the Escape of Sulphur Gases in the Manufacture of Sulphuric Acid.

By JAMES MACTEAR (*Chem. News*, xxxvi, 49).—This paper, which gives a full account of the method employed in determining the amount of sulphur gases escaping, together with the formulæ necessary for the calculations, is not suited for abstraction.

E. W. P.

Presence of Occluded Oxygen in Steels, especially in Bessemer Steel.

By SERGIUS KERN (*Chem. News*, xxxvi, 19).—The following two facts are well known to those who make cast-steel by the Bessemer process :—(1.) That on adding melted spiegeleisen to the metallic bath in the converter, a very high flame rises from the mouth of the apparatus; and (2), as the metal in the apparatus is thoroughly decarburised, which may be easily ascertained by the spectroscope, and as the percentage of carbon in the spiegeleisen coming from the cupola may be accurately determined, it is evident that the percentage of carbon in the steel obtained may be very easily and exactly predicated. The percentage of carbon is however always lower than it should be according to the calculations of the metallurgist. Some chemists explain this point by the occlusion of oxygen in melted steel, and some say that even solid steel contains oxygen in very minute quantities. Several experiments were made in order to ascertain the presence of oxygen combined with the steel in the metallic bath of the Bessemer apparatus before the addition of spiegeleisen. Five specimens analysed gave 0·054, 0·037, 0·025, 0·040, 0·031 per cent. of oxygen. The following method was used :—100 grams of the steel are placed in a combustion-tube, and the latter is connected with a potash apparatus containing a freshly-prepared concentrated solution of pyrogallic acid in potash. The potash apparatus having been carefully weighed, the combustion-tube is heated gradually, and through the tube and the apparatus nitrogen (dried) is passed. After an hour's ignition the operation is stopped and the potash apparatus weighed very quickly.

In conclusion, the author states his belief that in the above case the oxygen in the steel is in an occluded state, and even forms a certain chemical compound, very unstable however when heat is applied. It may perhaps be analogous to hydrogen-palladium, which some chemists regard as a chemical compound, while others consider it simply as a mechanical compound of palladium and hydrogen, the latter being merely occluded in the metal. D. B.

Method of increasing the yield of Potassium Carbonate from Molasses. By Camichel and Henriot (*Dingl. polyt. J.*, ccxxiv, 438).—Molasses which are to be fermented are not only neutralised with sulphuric acid, but further acidulated with an excess of about 6·3 per cent. of that acid, which, when the residues of the molasses are incinerated, remains in the form of potassium sulphate, thereby diminishing by an equivalent quantity the yield of carbonate. To prevent this loss, the authors employ—instead of the second portion of sulphuric acid, which serves only for acidulation—an extract of chestnut-bark, the active principles of which are tannic and gallic acids. The advantages of using this substance in place of sulphuric acid are that the fermentation and formation of yeast are facilitated; albumin and pectin principles are precipitated; the distillation does not yield any sulphuric acid residues; the apparatus used for distilling are less readily destroyed; and the yield of potassium carbonate is increased. The following analyses show differences in favour of this method:-

Constituents.	Molasses salts of the South.		Molasses salts of the North.	
	Sulphuric acid (1873).	Chestnut extract (1874).	Sulphuric acid.	Chestnut extract.
Potassium carbonate	19·55	33·30	36·93	47·03
Potassium sulphate......	19·95	15·30	16·02	6·37
Sodium carbonate	12·43	12·30	11·63	12·07
Potassium chloride......	16·70	17·70	13·64	16·29
Residue................	23·62	18·90	16·93	14·63
Water and loss..........	7·75	2·50	4·85	3·61
	100·00	100·00	100·00	100·00

(According to Savalle: *Appareil et Procédés nouveaux de Déstillation.* Paris, 1876, p. 21.) D. B.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Photometric Researches on Coloured Flames. By M. GOUY (*Compt. rend.*, lxxxv, 70—72).—The apparatus used in this research was described in *Compt. rend.*, lxxxiii, 209, and lxxxiv, 231. The following conclusions are drawn from its author's experiments:—When the thickness of the flame increases by a fraction $\frac{1}{n}$, the brilliancy increases $\frac{\kappa}{n}$; $\kappa = 0{\cdot}35$ for sodium, 0·45 for lithium, and 0·9—1·0 for calcium and strontium. The formula does not apply when $n<1$. With a reducing flame the brilliancy of the light of lithium, calcium, strontium, and barium increases, while that of sodium diminishes. With a large excess of air the spectrum of the former metals ceases to be visible, while that of sodium increases in brilliancy.

All salts of the same metal, when present in molecular proportions, give a flame of the same brilliancy, unless excess of hydrochloric acid is present. Exceptions to this rule exist in the case of the acid phosphates of calcium and strontium, which give a very weak spectrum; the nitrates of cacium and strontium also give a weaker spectrum than the other salts of those metals. All salts of the same metal give the same spectrum. If double the amount of salt be introduced into the flame its brilliancy is increased, and sometimes doubled; but the brilliancy is not directly proportional to the amount of metal present.

W. R.

Character of Flames charged with Saline Dust. By GOUY (*Compt. rend.*, lxxxv, 439).—Flames charged with saline dust exhibit spectra different from those usually given by the metals employed.

The author shows that there is at the base of the flame, produced by a mixture of air and gas, a very thin layer where the temperature is much higher than in the flame itself. In this layer many salts are dissociated, so that different spectra are obtained.

Platinic chloride gives at the base of the flame (by means of an arrangement of twenty small flames in a line) a spectrum formed by sixteen bands, grouped in couples, like those of cupric chloride, but wider and farther apart. Their right edge is sharply defined, and they fade away to the left; some are marked with dark equidistant lines. There are visible also some feeble rays, grouped in twos and threes. The author attributes this spectrum to platinous chloride.

C. W. W.

Effect of Light on Chemical Actions, and especially on Oxidations. By P. Chastaing (*Ann. Chim. Phys.* [5], xi, 145—224).—The object of this investigation is to compare the chemical action of the violet, green, yellow, and red parts of the spectrum: (1) upon salts of the metals and metalloïds; (2) upon organic compounds; (3) upon mixtures of organic compounds and metallic salts; to determine the radiations which cause the chemical actions accompanying fluorescence; to determine the action of light in the slow formation of ethers (these being taken as bodies which are produced with absorption of heat). The author gives the details of a great number of experiments in which he exposed various substances, usually for some days or weeks, to the action of the lights obtained by different coloured glasses (occasionally he used the direct light of the spectrum). He comes to the following conclusions:—

1. The chemical action of the spectrum upon binary compounds of the metals and metalloïds, and upon salts, is deoxidising at the violet end, while it is oxidising at the red end of the spectrum. If the ordinary curve which represents the chemical effect of the spectrum be taken for the violet end, it must be produced backwards and below the base line to represent the oxidising effect of the red rays, crossing the base line at a point between the lines D and E, for which point the action is neutral, that is the same as in darkness. The oxidising effect of the red is less than the reducing effect of the violet, so that white light has on the whole a reducing effect. Apparent exceptions to this general effect may be explained by secondary chemical actions.

2. The chemical action upon organic compounds is quite different, being entirely oxidising. It increases from darkness through the red to a maximum in the violet, and its numerical value being represented by 1 in darkness, is about 2 in red, and 3 in violet.

3. The chemical action upon mixtures of organic and inorganic compounds is in the same direction as the sum of the effects upon the two separately, but usually greater in intensity. If the oxidising effect upon the organic compound is greater than th[illegible] upon the salt, the total effect upon the salt may be a reducing one in all parts of the spectrum.

4. The rays which produce fluorescence are also those which produce the accompanying chemical effect.

5. The part played by light in the formation of ethers is at first feeble; it disappears almost entirely before the limit of etherification.

J. H. P.

The Influence of Sunlight, &c., on the Electrical Behaviour of Metals dipped in Water or Saline Solutions. By W. Hankel (*Annalen der Physik und Chemie* [2], i, 402—429).—A historical sketch of previous investigations on this subject is given. If a voltaic pile, consisting of the elements of zinc, copper, and water, and connected at its middle with the earth, be so arranged that the two poles are of equal strength, and if one of these poles be exposed to the sun's rays while the other remains in the shade, then the equality of the two halves of the pile is lost, and the gold leaves of the electrometer suffer a considerable divergence. This effect the author at first ascribed to the difference in temperature produced, but he subsequently found that the divergence due to artificial heat was owing to an increase in the tension of the pile, while that produced by light was due to a decrease in the tension, and he was therefore convinced that sunlight acted in a different manner to artificial heat. These results led him to investigate the action of light on metals placed in water or saline solutions. For this purpose one of two strips of the metal passed through a cork were placed in a porous vessel, so that the cork closed the mouth of the latter and kept the interior in darkness. The cell filled with water was then placed in a glass vessel likewise containing water, in which the other metallic strip was dipped. The two strips were connected with a galvanometer. By a proper arrangement the latter strip only could be exposed to the action of the sun's rays. The results obtained were as follows, that referred to being the action on the exposed strip:—

(1) *Copper dipped in water.* (a) *Metal freshly polished.* Negative; action increased from red to blue, and afterwards decreased in the violet rays. Similar effects were obtained when burning magnesium was the source of light. (b) *Metal partially oxidised.* Strongly negative; red rays have but a very small effect; in the yellow and green it was first positive, but soon afterwards negative; in the blue and violet it became negative. (c) As the amount of oxide on the surface of the metal increased, the change in the electrical condition due to light tended to become less negative, and finally strongly positive. From this it follows that the positive condition is produced by the action of the less refrangible rays on the metallic surface.

(2) *Copper dipped in a slightly acid solution of copper sulphate* (a) *Polished copper.* At first negative, afterwards strongly positive Action decreased from blue to null in the red. (b) *Oxidised copper.* Negative, action decreasing from blue to red end of spectrum.

(3) *Silver in water.* Negative. (4) *Silverised platinum in water.* Slightly positive, decreasing from the blue to the red. (5) *Platinised silver in water.* Very strongly positive, decreasing from blue to red, though still very strong in the latter. Ordinary gaslight produced a similar effect. With this metal stronger effects were obtained than with any other. (6) *Brass* in water behaved in a manner similar to oxidised copper. (7) *Tin in water.* Negative, decreasing from blue to red. (8) *Amalgamated zinc in solution of zinc sulphate.* Slightly negative; still smaller was the influence with ordinary zinc. (9) *Platinum in water.* Positive, decreasing from blue to red; the cleaner the platinum the smaller the effect.

Experiments with regard to the action of heat on the electrical condition of copper dipped in water showed that the heated copper was always negative, no matter whether it were polished or oxidised.

T. C.

On a Change in the Direction of the Polarisation Current after the Passage of an oppositely directed Galvanic Current.

By W. HANKEL (*Annalen der Physik und Chemie* [2], i, 429—430).—After successive charges of a voltaic battery with the two opposite electricities in proper proportions, it is well known that residual charges are obtained which, after some time, change their signs. The author finds that a similar change in the direction of the polarization current is produced after the passage of an oppositely directed galvanic current, as he had previously pointed out in a former communication. (See last abstract.) T. C.

Electro-capillary Phenomena. By BECQUEREL (*Compt. rend.*, lxxxv, 169—173).—The author here continues his observations on the electro-capillary actions between solutions communicating by narrow channels. Thus, when a cracked glass tube containing solution of sodium sulphide was plunged into solution of bismuth chloride, the sulphide first formed near the crack was afterwards reduced to the metallic state by the electro-capillary current, which thus finally prevailed over the chemical affinities. When certain metallic solutions were similarly placed in cracked tubes containing also pulverulent materials, such as sand, powdered charcoal, or quartz, the electro-capillary actions, gradually extending over the surfaces, were capable of ultimately producing a metallic deposit throughout the whole mass. R. R.

Electrolysis of Sulphurous Acid. By A. GUEROUT (*Compt. rend.*, lxxxv, 225—226).—In the electrolysis of an aqueous solution of sulphurous acid, the action does not consist, as it might seem, of a simple decomposition into sulphur and oxygen. The decomposition of H_2SO_3 resembles that of a salt; the H_2 going to the negative pole, where it reacts on a fresh portion of the acid, thus:—$4H_2 + H_2SO_3 = H_2SO_2 + H_2O$. This equation agrees with the observed facts of the formation of hyposulphurous acid (H_2O_2S), and the accumulation of combined sulphur at the positive pole. The deposit of sulphur, which occurs at the negative pole when the current is powerful, is explicable by the immediate decomposition of the concentrated hyposulphurous acid first formed there. R. R.

Diamagnetism of Condensed Hydrogen. By R. BLONDLOT (*Compt. rend.*, lxxxv, 68—69).—Becquerel and Faraday both classed gaseous hydrogen among diamagnetic bodies. It is known that palladium is weakly magnetic. It is, therefore, to be expected that the alloy of palladium with hydrogen should be rather less magnetic than palladium itself. The opposite is, however, the case, as was shown by Graham. Wiedemann supposed this to be due to the presence of iron oxide in Graham's sample of palladium, which, when reduced by the nascent hydrogen, would necessarily increase its magnetic properties. The author has re-investigated the question, measuring the magnetism by torsion, and found in every case palladium charged with hydrogen to be much less magnetic than pure palladium. From this it follows that solid hydrogen possesses comparatively strong diamagnetism. W. R.

New Experiments on Thermal Expansion. By P. GHATZEL (*Ann. Phys. Chem*, clx, 497—514).—These experiments were made with an instrument constructed by Herr Fuess, of Berlin, the details of which are briefly as follows:—A massive pillar stands at one end of a plate or base, and carries at its upper extremity and overhanging the base a solid arm; this whole support, forming three sides of a rectangle, is cast in one piece. The base plate carries also a triangular steel bar, fixed vertically, on which slides a horizontal arm, carrying at its end a vertical micrometer screw. The bar, whose expansion is be measured, is also placed vertically, with its lower end resting on the upper extremity of the micrometer screw, a small piece of ivory being interposed. On the upper end of the bar is a similar piece of ivory, which presses against the lower end of a short steel rod. This rod, which is capable of vertical motion, is bevelled at its upper extremity, so as to form a chisel edge, and is placed face to face with a similar steel rod fixed to the upper arm of the cast-iron support; the two edges meet like those of a pair of shears, and between them is a suitably-arranged lever, with a very long arm moving along a scale. When, therefore, the bar which is to form the subject of the experiment, is heated by means of a steam-jacket, the lower edge of the species of shears rises, depressing the point of the lever. When the expansion has reached its maximum, and the point of the lever no longer alters its position, the micrometer screw is turned round, thus lowering the bar, with the chisel resting upon it, until the lever has assumed the position which it occupied before the temperature was raised; the number of turns given to the screw gives, of course, the increase of length of the heated bar.

It is worthy of notice that a lever thus arranged is so sensitive that a few grams placed on the arm of the cast-iron support (which is 4 centimeters thick), bends it sufficiently to move the lever.

The greatest difficulty experienced in making the observations was due to the circumstance that, after the expansion had reached its maximum, and while the temperature of the steam-jacket remained constant, the point of the lever began to rise, indicating a contraction of the metal bar. This movement of the lever was very noticeable with a bar of cadmium—a metal whose co-efficient of expansion is relatively great. The author attributes it to the gradual rise of temperature of the iron pillar forming the main support, and states that the difficulty was obviated by sheltering the pillar from the heat.

The numbers obtained for the co-efficients of expansion of steel, iron, copper, zinc, aluminium, lead, and cadmium, differ considerably in the seventh decimal place from those lately given by Fizeau.

It was always observed that the metal bars on cooling, after being heated, did not assume exactly their former length, but became shorter, and that when they were again heated, the length again differed. The following table gives an example of this in the case of steel; the second and third columns give the readings of the screw-head before and after changing the temperature, each division being equal to a vertical movement of the screw of 0·005 mm. The fifth column gives the expansion calculated from each change of length; the steel bar was 10 centimeters long:—

Difference in temperature.	Readings of Screw.		Difference.	100 times Coefficient of Expansion.	
	Before.	After.			
84·0°	17·0	33·9	16·9	—	Heated.
83·8	33·9	11·7	22·2	0·001324	Cooled.
83·4	11·7	31·8	20·1	0·001199	Heated.
83·4	31·8	10·0	21·8	0·001302	Cooled.
83·4	10·0	30·0	20·0	0·001199	Heated.
83·4	30·0	8·4	21·6	0·001295	Cooled.
83·4	8·4	28·7	20·3	0·001217	Heated.

It is suggested that these variations are due to the bar being in a state of tension from forging, and that this tension tends to disappear when the bar is alternately heated and cooled.

In measuring the coefficient of expansion of various woods, the wooden rods were enclosed in a glass cylinder, thus protecting them from the action of the steam; they were dried in a vacuum before being used. The same variation in successive measurements of the expansion was observed as in the case of the metals. This may be partly due to absorption of moisture from the atmosphere during the cooling, and its subsequent expulsion by heating. The following table gives the mean value of the expansion from 0° to 100°, and for various kinds of wood; the expansion measured was that in the direction of the fibres. The measurement of the expansion perpendicular to the direction of the fibres is beset with great difficulty, owing to the effects caused by absorption of moisture:—

Maple	0·000502	Red beech	0·000716
White beech	0·000604	Pear	0·000721
Rosewood	0·000608	Oak	0·000746
Pine	0·000608	Poplar	0·000761
Box	0·000623	Mahogany	0·000784
Elm	0·000635	Ash	0·000951
Alder	0·000699	Ebony	0·000970

F. D. B.

On the Vapour-tensions of Homologous Series, and on Kopp's Law of Constant Differences of Boiling Points. By A. Winkelmann (*Ann. Phys. Chem.* [2], 430).—For liquids which belong to the same homologous series, Kopp's law states "that the boiling points at the atmospheric pressure form an arithmetical series, *i.e.*, that the differences of boiling points for the pressure of the atmosphere are constant." He did not, however, extend his investigations to pressures which are greater or less than that of the atmosphere, though he pointed out that the differences of boiling points were dependent on the pressure (*Ann. Chem. Pharm.*, xcvi, 32 (1855)).

Assuming the general truth of Kopp's law, the author shows that a simple relation can be derived from it for these differences of temperature at pressures other than atmospheric. This law, which takes the place of that of Dalton, the insufficiency of which has already been proved, is as follows:—" If, with a series of homologous liquids, we commence with temperatures at which the vapour-tensions are the same, then the differences of temperature which correspond with equal differences of pressure form an arithmetical series." Hence it appears that the differences of boiling points increase with an increase of pressure.

Dalton's law is apparently true only within certain limits, *i.e.*, when the value of *c* is sufficiently small, *c* being equal to (A—*a*), where A is the common difference of temperature at any pressure P, and *a* the common difference at any pressure, *p*.

The author also points out that commencing at temperatures which correspond with equal pressures, the rise of temperature which any member of a homologous series undergoes, is the greater the higher it is in the series.

The experiments of Landolt (*Ann. Chem. Pharm.*, *Suppl.* vi, p. 179) on the vapour-tensions of the lower members of the formic acid series, tend to confirm the truth of the above conclusions, from which it results that Kopp's law holds good for any pressure whatever.

T. C.

Some Fundamental Data in Thermo-Chemistry. By M. BERTHELOT (*Compt. rend.*, lxxxiv, 674—680).—The discrepant results obtained by different operators in the determination of the thermometric values of some of the fundamental reactions in thermochemistry, have rendered it imperative that these data should be redetermined.

Sulphur Dioxide.—The apparatus used in this experiment is not perfectly described; it is merely stated that the sulphur was burned in a porcelain crucible within a light capacious glass vessel, the latter being so arranged that the progress of the combustion could be watched, and the sublimation of sulphur on the production of sulphuric acid guarded against. About 0·8 gram of pure octohedral sulphur was burned in each experiment, the combustion being started by dropping upon the sulphur a fragment (2 mg.) of ignited carbon. The operation lasted ten or twelve minutes, and the heating of the water in the calorimeter four or five minutes. The mean of four determinations gave for the combustion of sulphur in oxygen, with production of gaseous sulphur dioxide, + 69·10 thermal units.* It was not found possible to avoid the formation of a trace of sulphuric anhydride, so that the true figure would be a little lower than that given above. The value of the corrections for cooling did not amount to more than four to five-hundredths of the total result.

This slight alteration in the thermometric value representing the heat of formation of sulphur dioxide, will of course more or less affect all calculations in which it is employed.

Hydrobromic Acid.—Favre and Silbermann, and more recently Thomsen, have determined the heat of formation of hydrobromic acid from the amount of heat evolved in the decomposition of potassium bromide by means of chlorine. Both of them obtained the same number, + 28·4, for a dilute solution of the gas. The author finds that the mean number + 27·2 represents the heat evolved by the reaction of bromine with a weak solution of sulphur dioxide, from which he calculates that in dilute solution hydrogen and liquid bromine disengage +.29·5, and hydrogen and gaseous bromine + 33·1 units. Knowing the heat of solution of gaseous hydrobromic acid to be +20·0 units, the following values result: H+Br liquid = HBr gas, +9·5 units; H+Br solid = HBr gas, +9·4 units; H+Br gas = HBr gas, +13·5 units.

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* Berthelot's heat-unit, or calory, is the kilogram-degree, *i.e.*, the quantity of heat required to raise the temperature of a kilogram of water by 1° C.

Hydriodic Acid.—By operating in the same manner as described in the case of hydrobromic acid, the number + 10·9 was found to represent the reaction of iodine with sulphurous acid. From this number may be calculated, as before, +13·2 units for the combination of hydrogen with solid iodine in dilute solution, and +18·8 units for hydrogen with gaseous iodine also in dilute solution. The heat evolved by the union of hydrogen with iodine, with production of gaseous hydriodic acid, then becomes, H + I solid = − 6·4 units; H + I liquid = − 4 5 units; H + I gas = − 0·8 units.

The numbers which express the thermic formation of the three hydracids from their *gaseous* elements are, HI = − 0·8; HBr = +13·5; HCl = +22·0 units, or values very nearly in the proportion of 1 : 2 : 3.

Bromic Acid.—By reducing potassium bromate with sulphurous acid in presence of a large excess of hydrochloric acid, Berthelot obtains the number − 24·8, representing the heat absorbed in the production of a dilute solution of bromic acid by the oxidation of liquid bromine. This result agrees perfectly with that obtained by Thomsen, by the reduction of the same salt with stannous chloride.

With gaseous bromine under similar conditions, the heat absorbed is − 21 1 units, and for the oxidation of hydrobromic acid in solution − 15·5 units. This latter number is practically the same as that obtained for chloric acid in solution, −16·8.

Hypobromous Acid.—Admitting that this acid in uniting with bases disengages the same amount of heat as hypochlorous acid, namely, + 9·5 units, the experimental results show that by the oxidation of liquid bromine in dilute solution, −6·7 units are absorbed, and by the oxidation of gaseous bromine −3·0 units. The heat of formation of hypochlorous acid is also negative, namely, −2·9 units. J. W.

Heat disengaged by the Union of Sulphuric Acid and Water. By M. CROULLEBOIS (*Compt. rend.*, lxxxv, 617—619). Also by M. BERTHELOT (*Compt. rend.*, lxxxv, 651).—The first paper is a purely theoretical one, and the result arrived at is stated in the second paper to disagree with the observed phenomena. Berthelot refers to *Ann. Chim. Phys.* [4], vi, 303 and 307, where a formula is established, the correctness of which has been verified in hundreds of cases.

R. R.

Heat disengaged by Combination in the Gaseous State: Anhydrous Acids and Water.

By M. BERTHELOT (*Compt. rend.*, lxxxiv, 1467—1472).—Three combinations are studied in this paper, viz., (1) anhydrous nitric acid and water—

$$NO_5(2\,v) + HO(2\,v) = NO_6H(4\,v).$$

(2) Anhydrous acetic acid and water—*

$$C_4H_3O_3(2\,v) + HO(2\,v) = C_4H_4.O_4(4\,v).$$

(3) Anhydrous chloral and water—

$$C_4HCl_3O_2(4\,v) + H_2O_2(4\,v) = C_4H_2Cl_3O_2,H_2O_2(8\,v).$$

1. The heat disengaged by the synthesis of nitric acid in the liquid state is found to be + 5·3 (*Ann. Chim. Phys.* [5], iv, 171). The heat of vaporisation of the hydrous acid has been found to be 7·18° by the ordinary method, and by another method, namely, passing the acid vapour directly into the water of a calorimeter, to be +7·33°; while for NO_5 +2·42 was found, the temperature of vaporisation of water at 100° having been found by Regnault to be +4·82. Therefore the sum of the heats of vaporisation of the two components equals 7·24, while that of the compound equals 7·25. From this it appears that the heat of union of gaseous NO_5 with water-vapour to form gaseous nitric acid is +5·3, or practically the same as for the liquid acid.

The author then compares the heat disengaged in the formation of nitric acid with that in the formation of the halogen-acids, and also, having determined the fusing point of monohydrated nitric acid to be −47°, he finds the heat developed by the union of solid NO_5 with solid HO to form HNO_6 to be + 1·1, which, however, he does not advance as a very trustworthy result.

2. *Synthesis of Acetic Acid.*—For this he has found, by methods similar to those used for nitric acid, that the heat of union for the liquids is +6·95, while for the gaseous bodies $C_4H_4O_3 + HO = C_4H_4O_4$, +7·88, that is, an increase of one-eighth in the heat of combination.

In conclusion the author expresses his opinion that these reactions may be represented more clearly in the equivalent than in the atomic notation, and that it is by no means one of the least faults of the new notation to have discarded the simple idea of anhydrous acids and bases, or, in other words, to suppress or complicate a whole series of positive facts and relations determined by direct experiment, because the new method is found to be incapable of explaining them.

J. M. T.

Note by Abstractor.—No results are given of the reaction, mentioned at the beginning of the paper, of chloral and water.

Thermal Conditions of the Formation of Chloric Acid and the Chlorates.

By M. BERTHELOT (*Ann. Chim. Phys.* [5], x, 377—

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* $H = 1$; $O = 8$; $C = 6$.

387).—The author continues the researches of Thomsen and others on this subject, and states his preference for the employment of a definite crystallised salt as the basis of this investigation. His results have been obtained by experiments upon pure barium chlorate, $Ba(ClO_3)_2$, his method being to reduce weighed quantities of the salt in aqueous solution by an aqueous sulphurous acid of known strength.

(1.) As a mean of six observations of the direct action $Ba(ClO_3)_2 + 6SO_2 + 6H_2O = SO_4Ba + 2HCl + 5SO_4H_2$, he obtains 214·3 units (kil.-degrees) for the heat disengaged by equivalent weights. The reaction $H_2SO_4 + Ba(ClO_3)_2 = BaSO_4 + 2HClO_3$ gives − 4·6 (units). Hence, for the reduction of the free acid the amount is (214·3 − 4·6) = 209·7 (units). Thomsen obtained 206·3 (units).

(2.) For the formation of the acid he obtains the thermal equation $Cl_2 + O_5 + H_2O = 2HClO_3$: − 14·1 (units), the calculated absorption being 12 units. Hence for the direct formation from its elements the equation $H_2 + Cl_2 + 3O_2 = 2HClO_3$: + 22·5 (units). (The author assumes − 12° (units) as the thermal equivalent of the preceding equation, and + 34·5 (units) as that of the equation $H_2 + O = H_2O$).

(3.) For the resolution of the acid into hydrochloric acid and free oxygen, the equation $HClO_3 = HCl + 3O$ the result is +16·8.

(4.) The same disengagement of heat attends the resolution of the chlorates in solution into chlorides and free oxygen, since the thermal evolution determined by the union of hydrochloric and of chloric acids with bases is seen from the following determinations to be sensibly the same.

Solution.	HCl.	$HClO_3$.
K_2O........	+ 13·7 (units).	+ 13·7 (units).
Na_2O	+ 13·7 „	+ 13·7
BaO........	+ 13·85 „	+ 13·8

(5.) Calculating for the heat of solution of the chlorides and chlorates, he obtains + 11·0 (units) for the thermal factor in the equation of resolution of the solid potassium chlorate. For $Ba(ClO_3)_2$ he obtains 12·6 (units), and for $NaClO_3$, 12·3 (units).

(6.) From these data he calculates + 3·66 (units) as the excess of heat evolved (for each atom of O) in a combustion effected by means of solid potassium chlorate, over that evolved in combustion in free oxygen.

(7.) For the formation of potassium chlorate from its elements he obtains + 94·6 (units); for sodium chlorate, 85·4 (units).

(8.) The author proceeds to consider the thermal factors in the equations expressing the three modes of action of gaseous chlorine upon solutions of potash. (1.) In the formation of *hypochlorite* the disengagement of heat amounts to + 76·2 (units) for equivalent weights of the reagents. (2.) The union of the same reagents to form the *chlorate* causes an evolution of heat = + 94·2. (3.) The formation of *chloride* and liberation of free oxygen disengages +111·0 (units). The numbers obtained by the author for sodium and barium differ but very slightly from the above.

These quantities, indicating, as they do, three stages of progressively increasing stability—from hypochlorite to chlorate, and thence to free oxygen—entirely conform to the chemistry of these bodies. Nevertheless the author joins issue with Thomsen respecting the conclusions to be drawn from these facts. The latter has stated that "of several possible reactions, that will take place at the lowest temperature which disengages the least amount of heat." In objection to this it is urged that the resolution of potassium iodate into the chloride and free oxygen—a parallel reaction, therefore—is attended with the *absorption* of 43·3 (units); and hence that in the case of the action of iodine upon potassium the reaction which occurs at the lowest temperature is that which disengages the greatest amount of heat. On the other hand, the author has proved that the formation of the hypoiodite precedes that of the iodate, and disengages a smaller quantity of heat. Thus the parallel reactions of iodine and chlorine upon the alkalis yield discordant thermal results.

(9.) The author discusses the thermal relations existing between the members of the series of oxides of chlorine, iodine, and nitrogen respectively, showing that the thermal maxima and minima are independent of the maxima and minima of oxidation: hence the extreme difficulty of generalising the relations between the quantities of heat disengaged and absorbed and the multiple proportions of the successive combinations of two elements.

(10.) Mention is made of unsuccessful attempts to extend this inquiry to chlorous and perchloric acid: and, finally, that the absorption of heat attending the solution of potassium perchlorate (*i.e.*, for $KClO_4$ dissolved in 100 times its weight of water at 23°, a quantity = — 12·13 (units), is greater than in the case of any known salt.

C. F. C.

Thermo-chemistry of Chloral and its Hydrate. By M. Berthelot (*Compt. rend.*, lxxxv, 8—14).

—The author measured the heat disengaged by the solution of chloral and its hydrate in water, by the action of alkalis on these two bodies, and on insoluble chloral. He also determined the specific heat and heat of vaporisation of the two bodies, and the fusing point of the hydrate. From the above he determines the heat disengaged by the combination of chloral and water at all temperatures, and in the solid, liquid, and gaseous conditions.

Solution.—C_2HCl_3O anhydrous (1 pt. +80 pts. H_2O) + water at 16° gave + 11·88° for 147·5 grams. In dissolving $CHCl_3O.H_2O$ in water at various temperatures, he finds that at 13° the heat disengaged = 0°.

Action of Alkalis.—In decomposing chloral in various solutions by means of potash, he finds that on an average 13·15° are developed.

Insoluble Chloral.—When insoluble chloral is treated in the cold with dilute potash solution, $C_4HCl_3O_2$ (insol.) + KHO (dil.) = $CHCl_3$ (dissolved) + CHKO gives 16·16° instead of 11·88 + 13·15 = 25·03 given off by pure chloral; so that the conversion of anhydrous chloral into the insoluble variety gives out 8·87°.

Specific Heat of Anhydrous Chloral.—The author finds the average specific heat between 17° and 81° as 0·259, between 17° and 53° as 0·250.

Specific Heat and Heat of Fusion of Chloral Hydrate.—The average specific heat of the solid hydrate between 17° and 44° he finds as 0·206, and of liquid hydrate between 51° and 88°, 0·470, in the liquid hydrate the specific heat varying rapidly with the temperature. The heat of fusion of the hydrate amounts to 5·50 (kilogram-degrees) for 165·5 grams.

Heat of Vaporisation of Anhydrous Chloral.—The author describes two methods of determination, but gives the preference to the one in which the gases are condensed in a calorimeter by means of a spiral. He determines the heat of vaporisation to be 7·98 (kilogram-degrees).

Heat of Vaporisation of Chloral Hydrate.—The vapour is condensed directly in the water of a calorimeter, by means of special apparatus, which will be described elsewhere. This heat is found to be 21·90 (kil.-degrees).

Heat Disengaged by Combination of Anhydrous Chloral with Water.—This is calculated under various conditions of the components and the compound, by means of data obtained from the above experiments. The author concludes by stating that his experiments show that heat is disengaged by the action of gaseous chloral on water-vapour, which forms a gaseous compound; he considers, therefore, that gaseous chloral hydrate really exists, and that this is confirmed by Troost's experiments on dissociation tensions. J. M. T.

Dissociation of Gaseous Hydriodic Acid in presence of an Excess of one of its Elements. By C. Lemoine (*Compt. rend.*, lxxxv, 34—37).—On the same quantity of hydrogen the author has acted successively with $1, \frac{3}{4}, \frac{1}{2}, \frac{1}{4}$ of its equivalent of iodine, two series of experiments being recorded, one at high, the other at low pressures.

The results relatively to the pressures employed may be expressed by two distinct forms.

(1.) Immediately after the experiment the proportion of free hydrogen remaining to the total hydrogen introduced may be calculated; when pure hydriodic gas has been taken, if this relation be 0·24, then 0·24 of gas has been decomposed.

(2.) From this the author calculates the relation of the dissociated to the *possible* hydriodic acid, and gives a numerical table of his results.

He finds that for small pressures the equilibrium is rather slow in establishing itself, but that the pressure of the gas, that is to say, the attraction of the molecules of iodine and hydrogen makes but a small change in the extent of the limit: this he has already found for equal numbers of equivalents. There is no indication of abrupt change in the extent of the limit when a change is made in the proportions of the two bodies.

The most important result is the stability given to the combination by an excess of one of the elements; thus on mixing gaseous hydriodic acid with increasing quantities of hydrogen, the amount of acid dissociated may diminish by about one-half. Still, however, the character of the dissociation seems to remain the same, whatever may be the inequality of the atomic proportions; for even an indefinite increase in one of the bodies does not lead to the total combination of the other: thus at 440°, for a constant quantity of hydrogen, there will be from

0·10 to 0·12 of hydriodic acid decomposed when only an infinitely small quantity of iodine is present.

The author thinks that the action of mass gives considerable stability to compound bodies during the period of dissociation, and that this must be taken into account in estimating the temperature of flames according as they are fed with a larger or smaller excess of one of the gases. This influence of mass in the dissociation of gases accords with certain analogous facts, as in the decomposition of insoluble salts by excess of sodium carbonate, the conditions of which have been determined by Malaguti. Wurtz also, in determining the vapour-density of PCl_5 in presence of an excess of PCl_3, has found that the dissociation is considerably lessened. J. M. T.

Dissociation of Ammoniacal Salts in presence of Metallic Sulphides. PH. DE CLERMONT and H. GUIOT (*Compt. rend.*, lxxxv, 37—39).—The author found that, in the cold, manganese sulphide is dissolved by ammonium chloride, no decomposition however taking place, and the liquid not containing any trace of ammonium sulphide. At the boiling heat the action of the ammonium chloride is different, and the phenomena became more complicated. On boiling ammonium chloride with excess of manganese sulphide, ammonium sulphide was set free, and the liquor after filtration contained chlorine, manganese, and ammonia, but all the sulphur had disappeared. The filtrate afforded a double salt of manganese and ammonium, represented by the authors as having the composition $MnCl_2(NH_4Cl)_{16} + H_2O$. On pushing the reaction of ammonium chloride on manganese sulphide to its extreme limits, no further formation of the double salt was observed, a different reaction taking place. The facts which the authors have observed tend to afford an explanation of the difficulties frequently met with in the determination of manganese by ammonium sulphide in presence of ammoniacal salts. The ammoniacal salt, according to the authors, dissolves manganese sulphide, but without decomposition in the cold. On applying heat, however, the acid set at liberty in consequence of the dissociation of the ammoniacal salt, decomposes a corresponding quantity of manganese sulphide, forming a soluble manganese salt, which is precipitated only on the addition of a fresh quantity of ammonium sulphide. J. M. T.

Vapour of Chloral Hydrate. By L. TROOST (*Compt. rend.*, lxxxv, 32—34).—On the 9th April, 1877, the author published a paper showing that chloral hydrate could exist in the state of vapour, and that its equivalent was equal to 8 vols.* In May and June, Wurtz published similar experiments, which according to him led to the directly opposite conclusion, viz., that chloral hydrate could not be volatilised without being broken up into 4 vols. gaseous anhydrous chloral and 4 vols. water. At the commencement of his investigations, and merely for preliminary experiments, the author worked under the same conditions as Wurtz, and obtained the same numerical results as the latter; he concluded, however, that the method employed was deficient in accuracy. The results published in his former communication were obtained by the following method, which he believes to be the best. A carefully measured volume of pure potassium oxalate dried in a vacuum is placed in a Hofmann's tube, the upper end of which gives a Torricellian vacuum of about 300° C.; the apparatus is kept at a temperature of about 78° by means of alcohol-vapour. The salt being now in the best state for absorbing aqueous vapour, a known weight of chloral hydrate is introduced into the tube; in 15 minutes the pressure is found to be equal to the sum of the pressures calculated for the chloral hydrate and the vapour given off by the oxalate; therefore in this part of the experiment no appreciable absorption has taken place. The author then gives a table showing the slight variations taking place in the pressure. From his results he concludes that these latter experiments, like the former, show that the oxalate is in presence of a gaseous atmosphere which yields to it only a very small quantity of aqueous vapour, and that very slowly. He answers the objection that the chloral present might prevent the absorption, by introducing 10 to 12 milligrams of water into the tube, whereupon about 60 per cent. is absorbed in 30 minutes, the rest being absorbed more slowly. Vapour of water, if produced in the decomposition of the chloral hydrate, would have been absorbed in the same way; that this is not the case he thinks is proved by there being no corresponding diminution of pressure observable in the tube. The author concludes by observing that he finds nothing to alter in the conclusions enumerated in his former paper.

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* Molecule of H_2, HCl, H_2O, &c. = 4 vols.

J. M. T.

On the Vapour of Chloral Hydrate. By L. TROOST (*Compt. rend.*, lxxxv, 400—402).—In this paper, which is a continuation of the last, and of the one an abstract of which is given at p. 273 of this volume, two methods for determining the volume-equivalent of substances in the state of vapour are applied to chloral hydrate.

(1.) By vaporisation of chloral hydrate in a space already containing vapour of water emitted by a hydrated salt. According as the tension of this water-vapour is or is not added to the tension of the hydrate, it may be determined whether the hydrate undergoes decomposition. It has already been shown by means of this experiment, that at 78° the hydrate exists in the gaseous state; the author now gives an account of some experiments proving that it also exists in this state at 99°. Tables of the results are given.

(2.) The inverse of the first. Chloral hydrate being first vaporised, a body capable of absorbing free water-vapour is then introduced. The author uses dehydrated potassium oxalate. The processes are minutely described, and lead the author to the same conclusions as before, namely, that chloral hydrate exists in the gaseous state, and that its equivalent corresponds to 8 volumes.* J. M. T.

Dissociation of Hydrocarbons by Means of Palladium Wire, and on the Similarity of these Phenomena to those of

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* 4 vols., if H_2 = 2 vols.

Catalysis. By J. COQUILLION (*Compt. rend.*, 1503—1504).—In a preceding notice, the author has pointed out that a palladium wire burns hydrocarbons when heated to redness in presence of oxygen. The object of the present experiments was to determine what takes place when the oxygen present is insufficient, or when the hydrocarbon is exposed to the wire alone. By means of an instrument called by the author a "grisoumètre," CH_4 or C_2H_4 is passed several times over a spiral of palladium wire heated to dark redness. No appreciable change in the volume takes place, but at a cherry-red heat after the gas has passed a considerable number of times over the spiral, an increase of volume takes place, and the ends of the palladium wire are found to have a deposit of carbon. The author repeated his experiments with natural marsh-gas, obtaining the same results.

He thinks that these point to a complete dissociation, C being deposited and H liberated. Berthelot has already indicated that CH_4 and C_2H_4 are decomposed by heat alone into hydrogen and acetylene. The author has not yet experimented on the latter gas, but thinks that it also will be decomposed. Platinum wire gave no results. From this the author concludes that in analysing hydrocarbons by means of palladium wire, care must be taken to have sufficient oxygen present to insure the complete combustion of the carbon and hydrogen. The dissociation appears to be reciprocal, as after a certain time the palladium becomes brittle, and its surface seen through a magnifying glass, resembles coke.* This action seems to be of a nature similar to that which takes place when NH_3 is passed over heated iron or copper wire. J. M. T.

On the Velocity of Chemical Action. By J. G. BOGUSKI and N. KAJANDER (*Deut. Chem. Ges. Ber.*, x, 34—37).—In the equation $d[CO_2] = kydt$, which connects the quantity of CO_2 evolved from a plate of marble in contact with acids with the concentration of the acid (y) and the duration of the action, the authors have determined the value of the coefficient, k, for hydrochloric, hydrobromic, and nitric acids to be inversely proportional to the mol. weights of the respective acids. Further, since the velocity of evolution of the gas, $v, = \frac{d[CO_2]}{dt} = ky$, it follows that this quantity also, is in each case inversely proportional to the molecular weight of the acid which determines the evolution, *i.e.*, in the special cases which have been investigated. C. F. C.

Note on Molecular Volumes. By F. W. CLARKE (*Amer. Jour. Sci.*, xiii, 292).—Some years ago the author pointed out some multiple relations connecting both elements and compounds; he found, for example, that a relation connected the alkali-metals with one another, and that the haloïd compounds of some of these metals had molecular volumes multiples of that of hydrogen. He had then, for this latter relation, the specific gravity determinations of only ten bodies, all of which had molecular volumes multiples of 5·5, the value assigned by Kopp to hydrogen in its liquid compounds at their boiling points. This relation is now extended to twelve other bodies.

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* This sentence is a literal translation of the original. It appears to the Abstractor that the term dissociation is used too generally in this paper.—J. M. T.

The following table shows in the 1st column the formula of the substance; in the 2nd the density, with authority given; in the 3rd the molecular volume found; in the 4th the same calculated; and in the 5th a theoretical density deduced from that volume.

I.	II.	III.	IV.	V.
LiF	2·295 Clarke	11·33	11·00	2·363
LiCl	1·998 Kremers..........	21·27	22·00	1·932
LiBr	3·102 Clarke	28·05	27·50	3·164
LiI	3·485 „	38·45	38·50	3·481
NaF	2·558 „	16 41	16·50	2·545
NaCl	2·145 Buignet..........	27·27	27·50	2·127
NaBr......	3·079 Kremers	33·45	33·00	3·121
NaI	3·450 Filhol............	43·48	44·00	3·409
KF........	2·096 Clarke	28·20	27·50	2·113
KCl	1·945 Kopp............	38·35	38·50	1·937
KBr	2·672 Playfair, Joule....	44·57	44·00	2·707
KI........	3·056 Filhol............	54·35	55·00	3·020
RbF	3·202 Clarke	32·64	33·00	3·167
RbCl......	2·209 „	54·78	55·00	2·200
RbBr......	2·780 „	59·53	60·50	2·735
RbI	3·023 „	70·29	71·50	2·972

The 3rd and 4th columns agree very closely, and the figures in the two columns of densities never differ by as much as 0·1.

The fluorides, except RbF, differ by 11 from the corresponding chlorides; rubidium fluoride differs by 22. It is worth noting that the five chlorides exhibit a curious relation; thus LiCl and NaCl differ by 5·5, NaCl and KCl by 11, KCl and RbCl by 16·5. This regular increase of difference suggests some law connecting them.

Sodium hydride, Na_2H, has a density of 0·959 and a molecular volume of 49·1, or very nearly 5·5 × 9. Iodine monochloride at 0° has a density of 3·263 and a volume of 49·8. At 98° (3 degrees below its boiling point), its density is 2·958 and its volume is 54·9. It thus, both when solid and when liquid, has molecular volumes multiples of that of hydrogen.

Silver and thallium compounds were not found to agree well with this relation.

Potassium tri-iodide has a density of 3·498, which gives a molecular volume of 120·1. 121 is an exact multiple of 5·5, and gives a theoretical density of 3·472.

Thus, including the silver and thallium salts, we know the densities of 26 substances. Of these 21 have molecular volumes multiples of that of hydrogen, 3 are doubtful, and 2 apparently disagree; the following law may, therefore, be safely asserted, subject to possible exceptions:—*Every compound containing only elements of the hydrogen group, has a molecular volume which is an exact multiple of that of hydrogen.*

C. W. W.

Absorption of Gases by Saline Solutions. By J. J. MACKENZIE (*Ann. Phys. Chem.* [2], i, 438—451).—Numerous measurements have been made of the absorption of gases in water and alcohol, whereas, with the exception of those of Saussure, they are completely wanting with regard to the absorption of gases in saline solutions. In the present paper, experiments are detailed bearing on this latter point.

The absorptiometer used (which differed little from that of Bunsen), is described at length, as well as the methods of experimenting and calculating the results from the observed data.

The absorptive powers of the solutions of the following chlorides for carbonic acid were determined:—Sodium, potassium, ammonium, calcium, strontium, and barium. The results obtained are expressed in tables, from which the following conclusions are drawn:—(1.) Saline solutions absorb less carbonic acid than an equal volume of water. (2.) The volume of gas absorbed decreases as the concentration of the solution increases. (3.) Different solutions possess different absorption-coefficients. The absorption-coefficient for potassium chloride, like its molecular weight, lies between those for sodium and ammonium chlorides, and that of strontium between those for barium and calcium chlorides. (4.) The coefficient varies with the temperature almost in the same manner as for pure water. The author is continuing his investigations.

[Almost contemporaneously with the foregoing paper there has been published a memoir by J. Setchenow on the absorption of carbonic acid by saline solutions. (*Mém. d. St. Pét.* (7), xxii.)] T. C.

Compressibility of Liquids. By E. H. AMAGAT (*Compt. rend.*, lxxxv, 27—29 also 139—142).—The author has investigated the compressibility of volatile liquids at temperatures above their boiling points, his investigations being carried out at the temperature of the air, at 100°, and at some intermediate temperatures. As the experiments were extended to 39 atmospheres, he was enabled to observe the influence of the limits of pressure at the same time. A detailed description of the apparatus used and of the method employed for correcting errors caused by expansion of the glass is given. The substances experimented on were chlorethylic and bromethylic ether, methyl- and ethyl-acetic ethers, methylic and amylic alcohols, the hydrides of amylene, hexylene, and heptylene, "benzine," acetone, chloroform, carbon disulphide, and ether. The last substances are those from which the largest number of results have been obtained. The following are the results in a tabulated form:—

Ether.

Temperature.	Pressures.		Coefficient of elasticity.
13·07°	4·88	7·67	0·000167
"	"	10·66	0·000168
"	"	13·90	0·000168
"	"	16·74	0·000167
"	"	19·78	0·000166
13·3	8·63	13·92	0·000168
"	"	19·87	0·000168
"	"	25·48	0·000168
"	"	30·59	0·000166
"	"	36·48	0·000165
25·4	8·46	34·22	0·000190
63·0	8·57	22·29	0·000300
78·5	8·63	22·34	0·000367
"	"	34·38	0·000363
99·0	8·60	13·50	0·000555
"	"	19·40	0·000550
"	"	25·35	0·000539
"	"	30·36	0·000528
"	"	36·50	0·000523

Hydrochloric Ether.

Temperature.	Pressures.		Coefficient of elasticity.
11·0°	8·48	34·24	0·000138
14·5	8·46	25·99	0·000148
15·2	8·70	37·22	0·000153
61·5	12·65	34·36	0·000256
62·0	12·66	32·84	0·000255
80·1	12·72	19·48	0·000360
"	19·48	34·42	0·000351
99·5	14·22	19·01	0·000513
		25·90	0·000507
		31·00	0·000495
		37·10	0·000487
		—	—
12·8	8·53	13·90	0·000156
		19·47	0·000156
		25·40	0·000154
		30·56	0·000153
		36·45	0·000151

The author concludes this first paper by saying that he intends shortly to publish further researches, and will discuss the results found in their general bearings, showing that there exists a satisfactory accordance between his numbers experimentally determined, and those deduced from the formulæ of the mechanical theory of heat.

In the second paper of the author on the same subject (*ibid.*, lxxxv, 139—142), he gives the results of his experiments with the following substances at 100°, and between the pressures of 9 and 38 atmospheres.

			Temperature of boiling water.	
Methylic alcohol	14·7°	0·000104	100·0°	0·000221
Ethylic alcohol	14·0	0·000101	99·4	0·000202
Amylic alcohol	13·8	0·000082	99·5	0·000154
Methylacetate	14·3	0·000097	"	0·000250
Ethylacetate	13·3	0·000104	99·0	0·000250
Amylene hydride	13·1	0·000172	99·4	0·000529
Hexylene hydride	13·8	0·000143	99·4	0·000356
Heptylene hydride	13·1	0·000122	99·5	0·000270
Benzine	16·0	0·000090	99·3	0·000187
Chloroform	"	"	"	0·000206
Sulphide of carbon	15·6	0·000087	"	0·000174
Acetone	14·0	0·000112	99·0	0·000276

From his results he infers that the compressibility of successive members of the paraffin series [carbures formèniques] decreases regularly, as we descend in the series, as much at 100° as at the ordinary temperature. *Benzine** is much less compressible than the hydride of amylene, which contains the same number of carbon atoms. In the series of alcohols and of their acetates, the direction of the variation, which is the inverse of that of the densities, may differ according to the temperature, and tends to become, at a high temperature, the same as in the series of carbides. The presence of sulphur, chlorine, or bromine tends to render the liquid bodies less compressible. Lastly if, for example, we compare the compressibility of hydride of amylene with that of ether or hydrochloric ether, the very probable conclusion may be formed that the first members of the paraffin series are the bodies having the greatest compressibilty in the liquid state. J. M. T.

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* The author's "hydrure d'amylène" is doubtless ordinary amyl hydride or isopentane, $CH(CH_3)_2—CH_2—CH_3$ (b. p. 30°), whence it may be inferred that his "*benzine*, qui renferme le même nombre d'équivalents de carbone," is either normal pentane, $CH_3—(CH_2)_3—CH_3$ (b. p. 37°—39°), or tetramethyl-methane $C(CH_3)_4$ (b. p. 9·5°).—ED.

Conclusions drawn from Experiments on the Action of Gases produced by the Explosion of Dynamite, in their relation to Meteorites and the circumstances attending the Arrival of these Bodies in our Atmosphere. By A. DAUBRÉE (*Compt. rend.*, lxxxv, 253—259 and 314—319). The experiments from which the author's conclusions are drawn, will be found in the *Compt. rend.*, lxxxiii, 115, and lxxxiv, 431, 526, 636.

From these he concludes that the compression of the air caused by the rapid passage of the meteorite through the atmosphere, not only produces the heat, the vivid incandescence, and the luminous trail which always forms so striking an accompaniment of the phenomenon, but also appears to be the principal cause of the rupture of the mass, and of the depressions found on the surface of the fragments, as well as the pulverisation of the fused substance on the surface. Most of the characteristics of meteorites may thus, according to his idea, be perfectly imitated on a small scale in the laboratory, by certain effects produced on different substances by strongly compressed and heated gases, and that by the accurate reproduction of the natural phenomena, we may obtain an explanation of them amounting to direct experimental evidence.

These resemblances between two orders of facts, appearing at first sight so different, seem to him as conclusive as those admitted to exist between the effects of electricity, whether developed in the ordinary electrical apparatus, or manifested in the higher regions of the atmosphere in the form of electrical discharges, as lightning, or the aurora borealis. The author thinks that, although before these experiments were made, the compression of the air had been looked upon in a general sense as the cause of the incandescence of meteors, experimental synthesis, such as he has carried out, was necessary, not only to justify that conclusion, and to give a thorough demonstration of it, but also to throw light upon the less known relations of the phenomena. He finally compares his own method of deducing conclusions from his experiments with that which Franklin pursued in his researches on atmospheric electricity. J. M. T.

Diffusion of Vapours through Porous Cells. By J. PULUJ (*Wien. Akad. Ber.*, lxxv, 401—418 and 639—664).—The only research previously made on this subject is that of Dufour on the diffusion of dry and moist air (*Bull. de la Soc. vaud. des Sciences*, xiii, 74).

There are three methods for carrying out experiments with reference to the diffusion of gases and vapours. (1.) That used by Graham, Bunsen, and others, in which an infinite volume of one gas, under constant pressure, is allowed to diffuse into a finite volume of another gas. (2.) That used by Graham in the case of nitrogen and carbonic oxide, in which finite volumes of two gases were allowed to diffuse into one another. (3.) In which two gases of infinite volume diffuse into one another under constant pressure. The author employs the last method, as it appeared best fitted to enable him to decide the question as to whether the porous partition acts as a system of fine holes in a thin wall, or of capillary tubes. He is, however, carrying out some experiments according to method (1) which he hopes shortly to publish. A description of the apparatus used, together with drawings, is given, for which reference must be made to the original. The following results are arrived at:—The proportion of the diffusing volumes remaining constant, the rate of diffusion of air towards aqueous vapour increases with the temperature. A similar result was also obtained with the vapours of ether and alcohol. This increase cannot be explained by a change in the volume of the spaces in the porous wall, as the latter contracts with rise of temperature.

Though in the case of alcohol and more especially of ether, the experimental numbers differ somewhat from the calculated, yet the author thinks that vapours obey approximately Graham's law for the diffusion of gases. Aqueous vapour, alcohol, chloroform, and ether were investigated.

A method is proposed for determining the relative moisture of the atmosphere by means of the rate of diffusion of aqueous vapour through a porous plate, in a manner similar to that by which the density of a gas may be calculated from its rate of diffusion. If $v =$ rate of diffusion, $S =$ tension of the vapour inside and s that outside the porous cell, and C a constant, then $v = CS \log\left(2 - \frac{s}{S}\right)$, and for a perfectly dry external atmosphere $v' = CS \log 2$. From these two equations we obtain $2^{\frac{v}{v'}}, = 2 - \frac{s}{S}$, and thence the relative moisture $F = 100\left(2 - 2^{\frac{v}{v'}}\right)$, or if t and t' are the times of diffusion into moist and dry air respectively, then $F = 100\left(2 - 2^{\frac{t}{t'}}\right)$. For the determination of F two observations are necessary, one into dry air and the other into the given atmosphere. The results obtained by this method agree very fairly with those observed simultaneously with August's psychrometer; as a rule, however, they are somewhat too low.

T. C.

The Physical Properties of Homologues and Isomerides. By F. D. Brown (*Proc. Roy. Soc.*, xxvi, 238).—I. *Density, Expansion, and Vapour-tension of Propyl and Isopropyl Iodides.*—A connection between the vapour-tension and rate of expansion of a liquid organic body is rendered probable by the researches of Kopp and others.

Their conclusions may be thus summed up :—

The atoms of the various elements entering into the composition of substances of the same chemical type, always occupy the same space when the tension of the vapour of the liquid is equal to the pressure exerted by a column of mercury 760 mm. in height. Hence the molecules of isomeric substances, which differ only in the arrangement of their constituent atoms, and not in their number or kind, must, when the tension is 760 mm., occupy the same space, or in other words, the molecular volumes of isomerides at their boiling points are equal. And, if this relation holds good when the vapour-tensions are equal to 760 mm., it must equally hold good at any other temperatures when the vapour-tensions are equal to any number, *n*, of millimeters, inasmuch as the ordinary barometric pressure of 760 mm. is merely a special circumstance due to the conditions under which our experiments are usually made.

In the present experiments, the boiling points, densities, rates of expansion and vapour-tensions were determined with apparatus, for the descriptions of which the original paper must be consulted.

Pure normal propyl iodide was prepared and fractioned; the first portion boiled at 102—102·25°, the second at 102·25—102·5°, and the third at 102·5—102·75° (temperatures uncorrected). The respective densities were—

I........	1·74772 at 20·79°;	1·78684 at 0°	mean density at 0° 1·78635.
II........	1·75035 at 19·27 ;	1·78641 at 0	
III........	1·74628 at 20·91 ;	1·78550 at 0	

The densities at 0° were calculated by the curve of expansions afterwards determined.

The boiling points and densities of three portions of pure isopropyl iodide are as follows :—

	Boiling point.		Density.
I.	88·6°—88·7°	uncorrected.	1·70526 at 19·80°; 1·74315 at 0°
II.	88·7°—88·8°		1·70506 at 20·14°; 1·74363 at 0°
III.	88·8°—89·0°		1·70457 at 21·09°; 1·74504 at 0

The mean density at 0° is therefore 1·744.

In the following table the densities are compared at those temperatures at which the vapour-tensions are equal :—

Vapour-tension in millimeters.	Boiling point of normal propyl iodide.	Boiling point of isopropyl iodide.	Density of normal propyl iodide.	Density of isopropyl iodide.	Difference of densities.
200	62·37°	50·50°	1·66704	1·64590	0·02114
300	73·51	61·33	1·64493	1·62359	0·02134
400	81·95	69·70	1·62808	1·60646	0·02162
500	88·84	76·44	1·61446	1·59246	0·02200
600	94·70	82·11	1·60250	1·58068	0·02182
700	99·83	87·13	1·59221	1·57035	0·02186
760	102·63	89·86	1·58670	1·56497	0·02196

The above numbers show that the relation between vapour-tension and expansion, which had been rendered probable by Kopp's researches, does not exist; that the molecular volumes of the two isomerides at corresponding temperatures are unequal, that of the normal iodide being greater than that of the other by an almost constant quantity. This fact is in accordance with the modern dynamical hypotheses on the constitution of matter. Isopropyl iodide is more unstable than the normal iodide, its instability being probably due to the greater velocity of its molecules; and from this greater velocity would follow a greater mean distance between the molecules.

The author has also made a series of experiments on the vapour-tension of ordinary propyl alcohol.

The curve representing these observations intersects that which expresses the tensions of normal propyl iodide, so that, whereas at 760 mm. the iodide boils at 102·5°, and the alcohol at 97·3°, at 370 mm. they boil at the same temperature, viz., 79·5°, and at 120 mm. the boiling point of the iodide is only 49·5°, whilst that of the alcohol is 56°.

This fact, which probably arises from the much greater latent heat of the alcohol, obviously renders useless all attempts to derive the boiling points of compounds from their constitution, so long as the boiling points at the ordinary pressure alone are taken into account.

C. W. W.

On the Quantivalence of Nitrogen. By A. LADENBURG and O. STRUVE (*Deut. Chem. Ges. Ber.*, x, 43—49).—The authors have investigated the compounds of triethylbenzylammonium prepared from triethylamine and benzyl chloride, and of benzyltriethylammonium prepared from benzylamine and ethyl iodide, with the view to establish the isomerism of the two compounds. In support of this they adduce the observation (1) that on adding hydriodic acid to the aqueous solution of the iodide of the former base, and evaporating on a water-bath, benzyl iodide is evolved continuously and in increasing quantity as the evaporation proceeds, whereas the iodide of the second base, when similarly treated, may be evaporated to dryness, entirely without evolution of benzyl iodide. (2.) That the platinochloride of the former base crystallises in prisms, apparently monoclinic, whereas that of the benzyltriethylammonium occurs in small tables, apparently belonging to the rhombic system; these, however, the authors have observed to pass on standing into a form identical with that first described. These facts are regarded by the authors as disproving the conclusions of Mayer and Lecco respecting the quantivalence of nitrogen.

C. F. C.

New Laboratory Apparatus. By F. FRARICHS (*Liebig's Annalen*, clxxxv, 193—204).—The apparatus described consists of (1) an arrangement for rapid filtration, adapted to both quantitative and qualitative operations; (2) a contrivance for determining vapour-densities, on which mercury is displaced by vapours and weighed; (3) an instrument for determining specific gravities. None of these can be explained intelligibly in an abstract without the help of the accompanying drawings.

J. R.

Inorganic Chemistry.

On some Combinations of Ammonium Chloride with the Chlorides of Potassium and Sodium. By E. CHEVREUL (*Compt. rend.*, lxxxv, 493).—Some cubical crystals composed of sodium and ammonium chlorides were found in guano; a similar compound was found in some seal-skin, a part of that guano.

To obtain similar compounds artificially, solutions containing ammonium chloride and potassium chloride in the following proportions were used:—

No. I. Equivalent weights of NH_4Cl and KCl.
No. II. 1 equivalent of NH_4Cl to 2 of KCl.
No. III. 1 equivalent of NH_4Cl to 3 of KCl.
No. IV. 2 equivalents of NH_4Cl to 1 of KCl.
No. V. 3 equivalents of NH_4Cl to 1 of KCl.

These compounds invariably crystallised in cubes of definite composition.

When sodium chloride was substituted for potassium chloride in solutions 1, 2, and 3, cubes were obtained, but 4 and 5 yielded needles.

C. W. W.

Notes on some Fluorides. By F. W. CLARKE (*Amer. Jour. Sci.*, [3], xiii, 291).—*Nickel Fluoride.*—This salt is prepared by dissolving nickel hydrate in aqueous hydrofluoric acid. On concentrating the solution, a granular mass of crystals separates out. They are represented by the formula $NiF_2.3H_2O$. The last portions of water are retained at 130°. Sp. gr. 2·014 at 19°. The anhydrous fluoride, NiF_2, has the sp. gr. 2·855 at 14°. Its molecular volume is 13·65.

When solutions of nickel and silver fluorides are mixed together and concentrated, the nickel salt usually separates out alone, the silver salt apparently decomposing. In one instance, however, pale apple-green needles, mixed with rhombohedrons, were obtained, which analysis showed to be a highly hydrated double fluoride of nickel and silver. The quantity was too small for accurate examination.

Zinc Fluoride.—The specific gravity of the hydrated salt is 2·567 at 10° and 2·535 at 12°, of the anhydrous salt, 2·566 at 17° and 2·612 at 12°.

The specific gravity of *lithium fluoride* is 2·295 at 21·5°, of sodium fluoride 2·588 at 14·5°, potassium fluoride 2·096 at 21·5°. The specific gravity of rubidium fluoride, determined on a very small quantity of material, is 3·102 at 17′. This salt is extremely deliquescent.

When silver fluoride is added to gold chloride, a pale-brown precipitate falls, which is a mixture of silver chloride and gold oxide: $2AuCl_3 + AgF + 3H_2O = Au_2O_3 + 4AgCl + 4HF$. The result is the same with platinum.

C. W. W.

The Constitution of Crystals of Barium Iodide. By J. THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1343—1345).—According to

H. Croft (*J. pr. Chem.*, 68, 402) barium iodide crystallises with 7 molecules of water, whilst G. Werther (*J. pr. Chem.*, xci, 331) found it to crystallise with only 2 molecules of water. Thomsen has now examined the point and confirms Croft, finding barium iodide to crystallise with 7 molecules of water. This is confirmed by the amount of change of temperature which ensues when the salt is dissolved in water. E. N.

Action of Hydrochloric Acid upon Metallic Sulphates. By A. B. PRESCOTT (*Chem. News*, xxxvi, 179).—1 gram of each sulphate was heated with 4·035 grams of aqueous hydrochloric acid containing 1·251 gram of HCl; the product was evaporated to dryness on the water-bath.

	Chloride formed.	Sulphate undecomposed.	Proportion of metal changed to chloride.
	grams.	grams.	
Ag_2SO_4	0·920	none	100
$HgSO_4$	0·915	,,	100
Bi_23SO_4	0·027*	0·836*	*
$Na_2SO_410H_2O$ ..	0·070	0·807	19·3
$Al_23SO_418H_2O$	0·042	0·895	10·5
$(NH_4)_2SO_4$ ...	0·083	3·898	10·2
$COSO_4$	0·072	0·914	8·6
$CuSO_45H_2O$ ...	0·019	0·964	3·6
$FeSO_47H_2O$ ...	0·013 (ferric chloride)	0·977	2·3
$CdSO_4$	0·017	0·981	1·9
$ZnSO_47H_2O$ ...	0·007	0·990	1·0
$PbSO_4$	0·007	0·992	0·8
$MnSO_44H_2O$ ...	0·004	0·992	0·8
K_2SO_4	0·006	0·993	0·7
$MgSO_47H_2O$ ...	0·003	0·995	0·5
Sb_23SO_4	none	1·000	—
$CaSO_4$	,,	1·000	—
$SrCO_4$	,,	1·000	—
$BaSO_4$	,,	1·000	—

M. M. P. M.

Vapour-density of Ammonium Sulphides. By A. HORSTMANN (*Compt. rend.*, lxxxv, 229).—When ammonia and sulphuretted hydrogen are mixed at temperatures from 50° to 80°, in any proportions whatever, no contraction of volume takes place. The author refers to *Compt. rend.*, lxxxiv, 1261, and to *Ann. Chem. Pharm. Sup.*, vi, p. 74. R. R.

The Decomposition of Ammonium Nitrate by Heat. By M. BERTHELOT (*Ann. Chim. Phys.* [5], x, 362—365).—Ammonium nitrate melts at about 152°, but it is only above 210° that it begins to give off a measurable quantity of gas; after this point the decomposition increases as the temperature rises; if the latter passes above 300° the reaction becomes explosive. These facts show that the decomposition is an exothermic one, as is also proved by the author's calorimetrical determinations. The quantity of nitrous oxide obtained is always less than what theory demands, owing to the volatilization of the ammonium nitrate. By means of an apparatus devised by him, and of which a drawing is given, the author finds that it is possible to sublime ammonium nitrate without notable decomposition, and he considers this to be of importance, as proving that this salt can be volatilized in nature.

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* After evaporation a residue [consisting of bismuth sulphate and chloride was found; on treating it with water, ·027 of chloride was found in the filtrate; the residue 0·836 is set down as undecomposed sulphate.

The author corrects an arithmetical error in his determinations of the heat evolved during the decomposition of ammonium nitrate, 20 units having been added by mistake to all the numbers (*Ann. Chim. Phys.* [5], vi, 188). T. C.

Oxidation of Haloïd Salts and of Sulphurous and Arsenious Acids. By M. BERTHELOT (*Compt. rend.*, lxxxiv, 1408—1412).— It is well known that moist potassium iodide absorbs ozone at ordinary temperatures, with production of iodate and liberation of a little iodine. The author finds that, under the same circumstances, potassium chloride and bromide likewise undergo oxidation, but the quantities of chlorate and bromate so produced are always very small. Thermic theory shows that the conversion of potassium iodide into iodate by direct union with ordinary oxygen corresponds with the disengagement of 44 kilogram-degrees, while the analogous reaction in the case of the chloride and bromide represents an absorption of 11 kilogram-degrees. The direct synthesis of potassium chlorate and bromate by the union of the haloïd salts with ozone is therefore effected at the expense of the supplementary energy residing in the ozone. Dry potassium iodide heated to 400° with dry oxygen in a sealed tube is found to yield iodate and a little free iodine. The substance also acquires an alkaline reaction, and the author conceives this to be due to the formation of a basic iodate, the probable existence of which is confirmed by the fact of a small but distinct disengagement of heat taking place when a solution of potash is added to one of neutral potassium iodide. The above-mentioned facts explain the difficulty of preparing potassium iodide free from traces of alkali and of iodate.

Though the combination of iodine with oxygen represents an exothermic action, the author was unable, under any circumstances, to effect the direct union of these two elements. Nor could he bring about a direct combination of sulphurous acid with oxygen, which is also an exothermic reaction. In the presence of water, however, the well-known reaction occurs, in which the result is the production of dilute sulphuric acid, but the heat disengaged in this reaction is double that represented by $SO_2 + O = SO_3$.

In the dry state arsenious acid cannot be made to absorb oxygen, but in solution this absorption may be observed, especially when heat is applied. A plate of platinum, however, partly immersed in a solution of arsenious acid acidified with hydrochloric acid, determines a marked absorption of oxygen, even at ordinary temperatures, and this absorption becomes rapid when heat is applied. In the cold one-fifth of the whole possible quantity of oxygen was found to have been thus absorbed in two months. These facts indicate that in estimating ozone by means of arsenious acid care must be taken to avoid the use of platinum. Silver is also inapplicable on chemical grounds.

R. R.

On a Phosphate of Lime Glass. By M. SIDOT (*Compt. rend.*, lxxxiv, 1501—1503).—In preparing some crystallised phosphides of copper, the author remarked that acid phosphate of lime could, by the action of heat, be transformed into a crystalline mass. This mass, called by him *pyrophosphate of lime*, on being exposed to a still higher temperature, undergoes partial decomposition, and becomes perfectly vitreous, its composition probably being $3CaO.PHO_5$. Its preparation is fully described. It is highly refractive, its index of refraction being 1·523, while that of crown glass is 1·525. Its sp. gr. = 2·6. Several objects, such as lenses and brilliants, have been prepared from it. The glass does not dissolve all metallic oxides as ordinary glass does, but dissolves the oxides of chromium and cobalt readily; by means of this solution the author has been enabled to imitate sapphires and peridotes. It is not attacked by acids in the cold, but boiling acids and potash act upon it. It is not acted on by hydrofluoric acid. It also makes an excellent and uniform enamel for crucibles and light porcelain.

J. M. T.

Some General Properties of Metallic Sulphides. By PH. DE CLERMONT and H. GUIOT (*Compt. rend.*, lxxxv, 404—405).—In some experiments made at the beginning of this year, the authors observed that certain metallic sulphides are decomposed by boiling water.

·870 gram of manganese sulphide heated in a retort with 500 c.c. of water gave in four successive distillations of 100 c.c. each, ·008 gram of sulphur, about one-fortieth of the whole sulphur combined with the manganese. The same experiment with ·880 gram of iron sulphide and 500 c.c. of water gave ·040 of sulphur, about one-tenth of all the sulphur combined with the iron.

The sulphides of antimony are also decomposed, sulphide of silver much less, while sulphide of lead shows no decomposition. A certain quantity of pure manganese sulphide was boiled for a long time with a large quantity of water in a flask, when it was found that the manganese had been oxidised, and that the solid residue, carefully washed, did not contain a trace of sulphur.

Manganese sulphide heated in a sealed tube with boiled distilled water at 100° gave, after heating for 15 hours and washing, a quantity of sulphur in the filtrate. The authors think that these experiments, showing sulphides to be decomposed by water at 100°, with formation of oxides and hydrogen sulphide, are further arguments in favour of the metallic nature of hydrogen. They have further found that damp carbon dioxide decomposes manganese sulphide at ordinary temperatures. Hydrogen does not decompose this sulphide at ordinary temperatures. The green hydrated sulphide is less easily decomposed by carbon dioxide than the one previously mentioned. Iron sulphide is also decomposed, metallic carbonates and sulphuretted hydrogen being produced in all these cases. The sulphides of lead, silver, and antimony do not seem to be decomposed by carbon dioxide. J. M. T.

On some Properties of Cadmium Sulphide. By A. DITTE (*Compt. rend.*, lxxxv, 402—404).—The author finds that cadmium sulphide is soluble in ammonium sulphide at ordinary temperatures, the solubility increasing with the temperature. A saturated solution of the sulphide in ammonium sulphide contains about 2 grams per litre; this solubility, though small, is greater than that of copper. He therefore recommends the use of the other alkaline sulphides for the separation of cadmium, as the potassium and sodium sulphides do not dissolve a sensible quantity at 50—60°. Should ammonium sulphide be used, it is necessary to look for cadmium in the filtrate from the sulphide produced. J. M. T.

Direct Reduction of Silver from its Sulphide. By R. SEGURA (*Chem. News*, xxxvi, 157).—Silver sulphide, whether in a finely divided state, massive, or as argentite, is completely reduced by mercury when the two substances are triturated together in presence of so much water as serves to form a pasty mass. M. M. P. M.

Solubility of Mercury in Water. By R. SEGURA (*Chem. News*, xxxvi, 158).—The author's experiments, which are, however, far from complete, show that mercury is soluble in water to the extent of 1 part in 10,000,000. M. M. P. M.

An attempt to form Double Salts of Silver Nitrate and other Nitrates. By W. J. RUSSELL and N. S. MASKELYNE (*Proc. Roy. Soc.*, xxvi, 357).—When a solution of silver and potassium nitrates, containing more than an equivalent of silver nitrate, is evaporated, a double salt of the composition $AgNO_3.KNO_3$ separates out.

With ammonium nitrate a similar compound is formed, an excess of silver nitrate, however, being unnecessary. With sodium, lithium, and lead nitrates no double salts are formed. On evaporating solutions containing equivalents of silver nitrate and of sodium or lithium nitrate, the more soluble silver salt separates out first; with lead nitrate this is not the case. This action appears to be due to the hygroscopic character of the salt, not to its solubility.

The crystals of the potassium and ammonium silver nitrates belong to the monoclinic system. Optical character negative; the optic axes lie in a plane perpendicular to the plane of symmetry, their divergence for red light being about 4° 25′, for blue light 13° 11′.

Crystals of strontium nitrate containing silver nitrate gave excellent measurements according with those of a cubo-octohedron.

C. W. W.

Crystallised Lead Carbonate formed on Objects found at Pompeii. By S. DE LUCA (*Compt. rend.*, lxxxiv, 1457—1459).—The bases of some bronze objects found at Pompeii were loaded with lead, which has now become converted into lead carbonate. In some of these the carbonate appears simply as an amorphous white mass; in others the amorphous mass is accompanied by carbonate in a translucid and compact state, with some incipient crystallisation; and in one case the remarkable circumstance is presented of the carbonate existing also in brilliant well-defined crystals, which must have been formed within a period of known limits. R. R.

Copper Phosphides. By M. SIDOT (*Compt. rend.*, lxxxiv, 1454—1456).—The paper describes the preparation of a phosphide of copper by the action of phosphorus on a solution of copper sulphate, It is a black substance, of specific gravity 6·35, not changed by air or water. At a red heat it melts, losing about 10 per cent. of its weight, and forming when cold a greyish-white, brittle, metallic looking substance. If, however, the heat be greatly raised, phosphorus is expelled, and the mass on cooling is white, and as hard as steel. When it has been several times fused and cast in ingots at different temperatures, it acquires very marked sonorous properties, especially if a little tin be added. These phosphides of copper present a ready means of incorporating known quantities of phosphorus with other metals. By heating the black phosphide in presence of phosphorus vapour, the author obtained a compound in fine hexagonal crystals having a metallic lustre. He obtained yet another crystallised phosphide of copper by heating in a crucible an intimate mixture of acid calcium phosphate, copper oxide, and charcoal. R. R.

Tendency of Manganese Sulphide to Oxidise. By PH. DE CLERMONT and H. GUIOT (*Compt. rend.*, lxxxv, 73—74).—Freshly precipitated manganese sulphide, when perfectly washed and dried between folds of bibulous paper, and left for three days in a vacuum over sulphuric acid to absorb moisture, becomes incandescent, and burns to sulphate and brown oxide of manganese, with evolution of sulphurous anhydride on exposure to air. The sulphides of iron, nickel, and cobalt do not exhibit this property. If pink manganese sulphide be boiled with ammonium chloride or tartrate for a sufficiently long time, it does not oxidise in air, even at 100°. The green sulphide, however, oxidises when treated in like manner. W. R.

Composition of Ferric Phosphate. By G. W. WAINE (*Chem. News*, xxxvi, 132).—To ascertain whether the precipitate formed by the reaction between ferric chloride and ordinary phosphate of sodium varies in composition accordingly as either salt is in excess, a view generally assumed by chemists, some pure crystallised ferric chloride (Fe_2Cl_6) free from ferrous chloride was prepared. The chlorination could be completed only by keeping the crystals in a bottle of chlorine gas exposed to light. Standard solutions of this salt and hydrodisodic phosphate (Na_2HPO_4) were prepared, and two samples of ferric phosphate made—(A.) By adding the ferric chloride to sodium phosphate in excess, with constant stirring. (B.) By adding sodium phosphate to ferric chloride. As the precipitates could not be washed by decantation, they were transferred to dialysers of parchment paper, which were suspended over large volumes of distilled water, renewed in a day or two, when it contained much salt. When completely washed, the precipitates were dried and ignited. The mass was next dissolved in hydrochloric acid, and the iron determined by potassium permanganate, after reduction to the ferrous state. For A 38·01 per cent. of iron was obtained, and for B 38·63 per cent. of iron. This would give for one molecule of PO_4 (= 95) in A, 1·04 as the atomic proportion of Fe (= 56); in B 1·06. This shows that the precipitate is essentially $FePO_4$, but that it has a tendency to contain a slight excess of iron, especially when precipitated in presence of an excess of iron. Two analyses of each sample by the magnesium process gave for one atom (56) of iron A (1) 1·004 mol. PO_4, (2) 0·97 mol. PO_4; and B (1) 0·91 mol. PO_4, and (2) 0·95 mol. PO_4.

When the precipitated ferric phosphate was exposed to air dried by sulphuric acid until its weight was constant, it was found to contain 2·65 molecules of water for each atom of iron present. This water was not entirely expelled at 250°. The precipitate appears, therefore, to be represented by the formula $2FePO_4.5H_2O$.

The author has endeavoured to determine phosphoric acid volumetrically, by mixing the solution with potassium iodide and starch, and adding ferric chloride until an excess was indicated by the liberation of iodine; but the mixture was far less sensitive to the action of ferric chloride than to that of chlorine. In attempting to use potassium sulphocyanate, acetic acid, which would of necessity be present in most determinations of phosphoric acid for practical purposes, was found to interfere seriously with the delicacy of the reaction.

D. B.

On certain Ammonio-cobaltic Compounds. By G. VORTMANN (*Deut. Chem. Ges. Ber.* x, 1451—1459).—The author continues his investigations of the compounds prepared by the addition of acids to a solution of cobaltous carbonate in ammonia and ammonium carbonate which has been allowed to oxidise by exposure to the air. The molecular ratio of ammonia (NH_3) to cobalt in these bodies being 8 : 1, they are distinguished by the prefix *octamine*.

Octamine-purpureochloride, $CO_2.(NH_3)_8.(H_2O)_2.Cl_6$, crystallises in small octohedrons of a deep violet colour, easily soluble in water. It is isomeric with Rose's praseochloride, $CO_2(NH_3)_8.Cl_6.2H_2O$. These two salts readily admit of conversion, the one into the other.

Octamine-roseochloride, $CO_2(NH_3)_8.(H_2O)_2.Cl_6.2H_2O$, is obtained as a bright red precipitate.

Octamine sulphate, $CO_2(NH_3)_8.(SO_4)_3.6H_2O$, crystallises in needles having a bright red colour.

By adding alcohol to the aqueous solution of this salt, a second *sulphate*, $CO_2(NH_3)_8.(SO_4)_6.4H_2O$, is deposited in small needles of a red-violet colour.

Acid carbonate, $CO_2(NH_3)_8.O_3.(CO_2)_4.2H_2O$, crystallises in long carmine-red prisms, soluble in water to a cherry-red solution.

Neutral carbonate, $CO_2.(NH_3)_8.(CO_3)_3.3H_2O$, crystallises in small rhombic plates of a red-violet colour, dissolved by water to a violet solution.

Lastly, a compound intermediate between the sulphate and carbonate, represented by the formula $CO_2(NH_3)_8.SO_4.(CO_3)_2.3H_2O$, crystallising in small copper-coloured plates.

The author has also obtained results confirmatory of those of Fr. Rose and C. D. Braun in their researches upon the praseo- and decamine-cobaltic compounds respectively. C. F. C.

Chloride of Cobalt-ammonium. By J. M. Merrick (*Chem. News*, xxxvi, 115).—By mixing a solution of cobalt chloride and ammonium chloride, and setting the mixture aside for some weeks to crystallise, a confused mass of crystals is obtained. The mass consists of ammonium chloride, in which large crystals of cobalt chloride are imbedded. The latter, when picked out and washed, give, upon testing, mere traces of ammonia, so that no double salt appears to be formed in this way. D. B.

Conversion of Chromic Hydrate and Chromic Chlorate into Chromic Acid. (*Dingl. polyt. J.*, ccxxv, 294—299.)—Balanche has shown (*Bulletin de Rouen*, 1876, 419) that Guignet's green, when treated with cold bleaching powder solution for some time, loses its green colour, almost all the chromium appearing in solution as chromic acid. This reaction was applied by Balanche, and some years before by Stein, to distinguish chromium oxide from other green colours on cotton.

Witz has shown (*ibid.*, 421) that Guignet's green is readily and completely dissolved by boiling bleaching powder solution. The presence of a little calcium oxide substantially retards the dissolving process. Excess of hydrochloric or nitric acid prevents solution; but by the addition of sufficient nitric acid to neutralise the calcium oxide present, the solution is facilitated.

Guignet's green and also chromic oxide, when suspended in water, can be oxidised by potassium permanganate, with or without the addition of soda-lye. Bohlig has applied this reaction to the assay of commercial chrome green. According to Witz, acid does not interfere, and the liquid may be warm or cold.

Guignet's green, fixed on cotton with albumin and treated with soda-lye, loses its colour on adding a little potassium ferricyanide; the deposited oxide of iron may be removed by adding sodium tartrate to the lye, when the cotton can be washed clean. Witz suggests the application of this to dyeing.

Storck and von Coninck have shown (*Bulletin de Rouen*, 1877, 43) that the green solution of chromium chlorate obtained by adding chrome alum solution to hot barium chlorate solution, then cooling and filtering, becomes orange-red as it evaporates on heating alone. If lead acetate is added to the solution before heating, the colour begins to change at 60°, and at 80° lead chromate is precipitated. In this manner a fixed chrome-orange dye was obtained on cotton after treating with hot lime solution.

According to Depierre and Perrey (*ibid.*, 1877, 45), this yellow is not very pure; by taking less lead acetate a better colour is obtained, but the goods are attacked.

The chromium chlorate solution can take up in the cold a considerable amount of freshly prepared, well pressed chromic hydrate, but neither the dry hydrate nor Guignet's green. After five or six days some chromic acid is formed. This change does not take place in the original chromium chlorate solution. J. T.

Researches on the Chromates. By A. Etard (*Compt. rend.*, lxxxv, 443).—When neutral potassium chromate is boiled with ammonium sulphate or chloride, ammonia is freely evolved and the liquid becomes acid. When, however, the warm solutions are mixed in equivalent proportions, long, brilliant, yellow prisms separate out on cooling. These crystals have the formula $(NH_4)KCrO_4.H_2O$, and are produced according to the equation $K_2CrO_4 + NH_4Cl = KCl + (NH_4)KCrO_4$. On boiling them with water, the following reaction takes place, $2(NH_4)KCrO_4 = 2NH_3 + H_2O + K_2Cr_2O_7$. The same salt is formed when potassium bichromate is dissolved in ammonia, the contrary reaction to the above then taking place: $K_2Cr_2O_7 + 2NH_3 + H_2O = 2(NH_4)KCrO_4$. Evidently this body and the body NH_2KCrO_3 (prepared by means of potassium chlorochromate) are in the relation of acid and amide, $NH_4KCrO_4 - H_2O = NH_2KCrO_3$.

As potassium chromate is isomorphous with the sulphate, the author attempted to prepare the double salts $SO_4M.CrO_4R_2.nH_2O$, analogous to the salts of the magnesium series, $SO_4M.SO_4R_2.6H_2O$; but, when equivalent weights of magnesium sulphate and potassium chromate are crystallised together, these salts are not formed. When two molecules of magnesium sulphate to one of potassium chromate are used, yellow, well-formed clinorhombic prisms are obtained, having the composition $(SO_4Mg)_2CrO_4K_2.4H_2O + 5aq$. This salt differs from those of the magnesium series by one molecule of magnesium sulphate and three molecules of water, and also by retaining four molecules of water at 100°.

It is remarkable that in this chromate, as well as in many sulphates, the water retained at 100° is in the proportion required by a salt containing in its molecule dehydrated sulphuric acid, $H_2SO_4.2H_2O$. When the sulphates of copper, zinc, or nickel are substituted for the magnesium sulphate in the above reaction, the same result is not obtained, the salt of the magnesium series being formed by the reaction, $2CuSO_4 + K_2CrO_4 = K_2Cu(SO_4)_2 + CuCrO_4$. C. W. W.

On Complex Inorganic Acids. By Wolcott Gibbs (*Amer. Jour. Sci.* [3], xiv, 61).—About twelve years ago Marignac described three acids obtained by boiling silicic hydrate with an acid tungstate of alkali-metal; the first two, silico-tungstic and tungsto-silicic, are both represented by the formula $12WO_3.SiO_2.4H_2O$; while the third, silico-decitungstic acid, has the formula $10WO_3.SiO_2.4H_2O$.

The author has generalised these results, and has prepared a number of new acids of complex structure.

Platinic hydrate, $Pt(OH)_4$, boiled with an acid sodium tungstate, yields two isomeric or metameric sodium salts of the formula

$10WO_3.PtO_2.4Na_2O + 25aq$; one of them gives magnificent olive-green crystals, the other fine honey-yellow prisms with adamantine lustre. They are readily soluble in water, and give flocky or sub-crystalline precipitates with the heavy metals and with the higher alkaloïds. The corresponding potassium and ammonium salts have respectively the formulæ

$$10WO_3.3PtO_2.4K_2O + 9aq \text{ and } 10WO_3.PtO_2.4(NH_4)_2O + 12aq,$$

but both belong to the yellow series.

Acid sodium molybdate also dissolves platinic hydrate, giving a deep olive-green solution, appearing red in thick layers. The only salt of this series as yet studied crystallises in amber-coloured plates having the formula $10MoO_3.PtO_2.4Na_2O + 29aq$, very soluble and giving sub-crystalline precipitates with many metallic solutions. The acids corresponding with all these salts may be obtained by treating the barium salts with sulphuric acid or the silver salts with hydrochloric acid. Nearly all the salts effloresce strongly, and the alkaline salts have a distinct acid reaction, showing that the limit of the basicity is higher than eight. Attempts to replace the platinum hydrate in these acids by zirconium, titanium, and stannic hydrates did not lead to very definite results. Silico-molybdic acid appears to be formed by boiling acid sodium molybdate with silicic hydrate, in colourless or very pale-yellow crystals.

About five years ago Scheibler described two phosphotungstic acids, containing respectively 6 and 20 molecules of WO_3 to 1 of phosphoric oxide. According to the author the 20-molecule acid has the formula $20WO_3.P_2O_5.8H_2O$, independently of water of crystallisation. Salts of this acid were also obtained, having the following formulæ:—

$$\begin{array}{lllll}
20WO_3 . & P_2O_5 . & Na_2O . & 7H_2O & + 16aq. \\
20WO_3 . & P_2O_5 . & 2BaO . & 6H_2O & + 18aq. \\
20WO_3 . & P_2O_5 . & 6BaO . & 2H_2O & + 44aq. \\
20WO_3 . & P_2O_5 . & 7K_2O . & H_2O & + 27aq. \\
20WO_2 . & P_2O_5 . & 8K_2O & & + 18aq.
\end{array}$$

All these salts have an acid reaction except the 8-molecule potassium salt; the author therefore considers this, provisionally, as the limit of basicity of this acid. This shows that it is not only the phosphoric acid that is saturated. Debray describes a 7-molecule silver salt which is evidently the analogue of the above 7-molecule potassium salt. Nearly all the phosphotungstates effloresce quickly in dry air. All but the first-mentioned sodium salt are colourless; and there is at least one ammonium salt which is precipitated as a white crystalline powder.

The corresponding arsenio-tungstic acid and its salts are easily obtained, and more or less decided indications of vanadio-tungstic and antimonio-tungstic acids. When sodium oxyfluotungstate, $WO_2F_4Na_2$, is substituted for the normal tungstate, splendid crystalline salts are obtained with both arsenates and phosphates; the corresponding molybdenum salts are not well defined.

The author thinks that the empirical formulæ of the platino-tungstates and platino-molybdates should be doubled, so as to bring them into the same series as the phosphotungstates, &c., *e.g.*, $20WO_3.Pt_2O_4.8Na_2O$ and $20WO_3.P_2O_4.8Na_2O$. Also that the well-known $\frac{3}{7}$-tungstates and molybdates, $3Na_2O.7WO_3$ and $3Na_2O.7MoO_3$ should be written $20WO_3.WO_3.9Na_2O$ and $20MoO_3.MoO_3.9Na_2O$. Also that Wöhler's salt, $WO_4Na_2 + W_2O_5$, may be represented by the formula—

$$16WO_3.4WO_2.7Na_2O.$$

C. W. W.

Mineralogical Chemistry.

Diamonds. By E. H. v. BAUMHAUER (*Annalen der Physik und Chemie* [2], i, 462—478).—The results obtained by Schrötter (*Wien. Ber.*, 1871, B, lxiii) and G. Rose (*Ber. Monatsber.*, Juni, 1872, and *Pogg. Ann.*, cxliii, 497) in their researches on diamonds do not agree in certain points either with one another or with the data obtained by previous investigators; the author has therefore undertaken some researches on this subject, with special reference to the different conditions in which the diamond is found in nature.

The diamond generally occurs in more or less completely colourless or slightly coloured crystals, but there is also found along with it a black or grey porous substance containing iron and lime, and leaving ·24 to 2·0 per cent. of ash; this is known in the trade as "Carbonado." Another modification is "Bord," which consists of translucent colourless or grey spheroïds. Both carbonado and bord are much harder than diamond, and are therefore employed for polishing the latter. The author has determined the specific gravity of these varieties and gives a table of results. From these and all other known results he believes that the specific gravity of pure diamond is not much below 3·52, and that of bord not much above 3·50; the specific gravity of carbonado, however, is much less than either, being about 3·20.

With exclusion of air the diamond can be heated to the highest temperatures without suffering any visible change or loss of weight. This is the result already arrived at by Morren, Schrötter, and G. Rose.

When diamonds are heated in an atmosphere of hydrogen, not only does no detrimental change take place, but the brilliancy is even sometimes considerably increased. A dark green, almost opaque diamond after heating, greatly increased in transparency and became violet. Brown diamonds in great part lost their colour. A rose-coloured diamond when heated did not deepen in colour, but on the contrary became colourless; after some time, however, the rose tint returned (*Pogg. Ann.*, cxxviii, 176). The author attempted by heat to convert grey diamonds into the more valuable rose-tinted ones, but without success.

On heating diamonds in air the surface becomes dull and opaque, while in oxygen the stone glows and burns with a brilliant light long before a red heat is reached. During the combustion the diamond is surrounded by a small flame of a blue or violet colour, though this experiment was repeated several times no blackening or conversion into coke was observed, even at the temperature of melted platinum; he therefore thinks the blackening or conversion of diamond into coke or graphite very doubtful, and that the opposite results arrived at by Jacquelain (*Ann. Chim. Phys.* [3], xx, 439) and Clarke (*Gmelin's Handbuch der Chemie*, 1843, i, 338), as well as by Silliman, Murray, Macquer, Siemens, and Rose were due to foreign substances or to the deposit of carbon on the diamond from the carbon points of the battery employed. When heated in an atmosphere of steam diamond undergoes no change; at a white heat it decomposes carbon dioxide very slowly, taking up half its oxygen.

The author intends trying the action of other gases. T. C.

Analyses of Brown-coal. By A. HILGER (*Liebig's Annalen*, clxxxv, 211—213).—The author has analysed various specimens of brown-coal and lignite from a bed occurring near Bischofsheim on the Rhön. He found them to contain from 61·74 to 76·43 per cent. of carbon and from 4·94 to 8·88 per cent. of hydrogen. The amount of ash varied from 4·6 to 10·4 per cent.; that of water from 8·7 to 15·2 per cent.

A large heap of refuse from former workings, which has lain for many years, was found to contain in various parts from 20 to 68 per cent. of ammonia-alum and from 10 to 78 per cent. of sulphur, mixed with clay and ferric oxide.

An efflorescence on the earthy layers separating the several strata of brown-coal was found to be keramohalite, or aluminium sulphate with 18 mol. of water. J. R.

Description of several Minerals. By F. PISANI (*Compt. rend.*, lxxxiv, 1509).—*Triphane from Brazil* has a general resemblance to cymophane, but with a lower degree of hardness. Easily cleavable; transparent; doubly refracting. Hardness 7, density 3·16. The plane of the optic axes is parallel to the plane of symmetry. The mineral decrepitates violently before the blowpipe, colouring the flame purple; melts to a white glass and gives off no water when heated. The analysis of the body gave—

			Oxygen.	Ratio.
SiO_2 ……	63·80	—	34	8
Al_2O_3 ….	27·93	—	13	3
FeO ……	1·05	0·23	4·22	1
MnO ….	0·12	0·02		
CaO ……	0·46	0·13		
Li_2O ……	6·75	3·61		
Na_2O ……	0·89	0·23		
	101·00			

Anthophyllite from Bamle in Norway.—This variety becomes white before the blowpipe, melting to a white enamel. The analysis is as follows:—

			Oxygen.	Ratio.
Silica	51·80	—	27·6	9
Al_2O_3	12·40	—	5·8	
FeO	3·67	0·8	12·2	4
MgO	27·60	11·1		
$Na_2O + K_2O$ ..	1·44	0·3		
Loss	3·00			

He has found also the following composition for snarumite:—

SiO_2.	Al_2O_3.	FeO.	MgO.	$K_2O + Na_2O$.	CaO.	Loss.
57·90	13·55	1·90	19·40	4·50	0·87	2·86

Tephroite from Langban in Sweden.—Ganomatite was the name given to a mineral from the above place which, among other oxides, was supposed to contain a certain proportion of lead. The author finds that this is the case, and that the grey mass supposed to be ganomatite is only a mixture of jacobite and a silicate containing much manganese. The specimens also contained a reddish-brown mica having one optical axis and containing manganese, and another laminated substance of a light yellow, striated on the faces, which appears to be a diopside. The analysis of tephroite gives—

			Oxygen.	Ratio.
SiO_2	31·70	—	16·90	1
MnO	47·70	10·7	17·10	1
MgO	9·48	3·4		
CaO	9·80	2·8		
FeO	0·80	0·2		
	99·48			

Igelström has analysed a silicate from Pajsberg under the name *hydrotephroite* containing more than 5 per cent. of water. The qualitative composition of the diopside mentioned above is that of pure diopside.

Pharmacosiderite from the Garomne Mine.—It occurs associated with adamine, letsomite, brochantite, olivenite, calcophylite, and mimetesite, in olive-green cubical crystals, sometimes modified by the faces of the tetrahedron.

J. M. T.

A New Anthophyllite from Bamle in Norway. By A. Des Cloiseaux (*Compt. rend.*, lxxxiv, 1473—75).—The mineral occurs in numerous brilliant needles of a yellowish-grey colour, semi-transparent, easily cleavable in the direction of the lateral faces of a rhomboïdal prism of about 125°—20′, and with difficulty in the direction of h′. These needles are very fragile. Its density = 2·98, according to Pisani. This small specific gravity, combined with differences of colour, &c., between it and the beautiful Konigsberg variety, seemed to point to the inference that the specimen under discussion was the type of purely magnesian anthophyllite. Pisani, therefore, analysed the specimen, the results being given in a paper in the last abstract, showing that the Bamle specimen is poor in oxide of iron (3·6 p. c.), rich in magnesia (27·6 p. c.), and contains, besides, a large quantity of alumina (12·0 p. c.), which makes it appear to be closely related to the gedrite of Dufrénoy and of the snarumite of Breithaupt. In conclusion, the author thinks that anthophyllite being essentially composed of silica, oxide of iron, and magnesia, is nearly allied, as far as its chemical composition goes, to the amphibole group, from which it is perfectly separated by the rhombic character of its crystals; a further similarity with the amphibole group consists in the large proportion of alumina the mineral may contain, and its marked tendency to pseudomorphism. J. M. T.

On a Fibrous Variety of Sepiolite from Utah. By A. H. CHESTER (*Amer. Jour. Sci.*, xiii., 296).—This mineral occurs, in a silver mine, in a vein cutting the rock strata nearly at right angles.

The following are the analyses of two varieties, one green, the other white:—

SiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	CuO.	MgO.	H_2O.	Moisture.
52·97	0·86	0·70	3·14	0·87	22·50	9·90	8·80
50·15	2·06	1·02	2·09	6·82	18·29	9·30	10·32

One-half of the water is driven off at 100°, but a full red heat is required to drive off the whole. The formula obtained (disregarding the water driven off below 110°), is $2MgO.3SiO_2 + 2H_2O$, which is that of sepiolite. In its blowpipe characters, it resembles sepiolite exactly, as well as in its behaviour with acids. C. W. W.

Identity of the so-called Peganite of Arkansas with the Variscite of Breithaupt and Callainite of Damour. By A. H. CHESTER (*Amer. Jour. Sci.*, xiii, 295).—A recent analysis of the so-called peganite of Arkansas shows it to be identical with variscite.

The following are the comparative analyses of the three minerals:—

	Peganite.	Variscite.	Callainite.
P_2O_5	44·35	44·05	43·31
Al_2O_3........	31·85	31·25	30·09
H_2O	23·80	22·85	24·04
Fe_2O_3........	—	1·21	1·86
MgO	—	0·41	—
CaO	—	0·18	0·70
	100·00	99·95	100·00

The peganite and callainite are calculated to 100 p. c., after deducting the insoluble residue of quartz:—

The formula $Al_2O_3.P_2O_5 + 4H_2O$ requires P_2O_5 44·80; Al_2O_3 32·49; and H_2O = 22·71.

The mineral occurs in crystalline crusts on quartz; rarely in distinct crystals belonging to the orthorhombic system. Colour, emerald-green to nearly colourless. Transparent to translucent and infusible, hardness = 4. Before the blowpipe it becomes opaque, friable, and of a deep purple while hot, lighter on cooling. C. W. W.

Analyses of Zinckenite, Tetrahedrite, Trachite, and Magnetic Pyrites. By A. Hilger (*Liebig's Annalen*, clxxxv, 205—209).—

Zinckenite.—This mineral, heretofore known to occur only at Wolfsberg in the Harz, has now been found in the Schwarzwald, near Hausach in the Kinzigthal. The sp. gr. of the specimen was 3·6. It contained lead, antimony, and sulphur, in the proportions required by the formula PbS_2S_4, together with iron and sulphur, (FeS_2).

Tetrahedri[illegible] (*Fahlerz*).—A specimen of this mineral from the Schappbachthal in the Schwarzwald, gave, on analysis, numbers agreeing with the formula $As_2(Sb_2,Bi_2)S_3$, $Fe(Ag_2,Zn,Cu_2)S$.

Trachyte.—A specimen of this mineral from Wolferlingen was found to contain in 100 parts :—

SiO.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_3O.	Na_2O.	P_2O_5.	H_2O.
59·87	22·52	0·32	2·52	0·13	2·5	0·46	4·42	5·78	0·3	2·24

together with traces of chlorine and sulphuric acid, and of lithium, barium, and strontium. Its sp. gr. was 2·68.

Magnetic Pyrites from the Todtmoos in the Schwarzwald was found to contain in 100 parts :—

S.	Fe.	Cu.	Co.	Ni.
40·46	56·58	0·54	0·48	1·82

After deducting the copper as CuS, and the cobalt and nickel as Co_2S_3, and Ni_2S_3, the remainder consists of 40·39 per cent. of sulphur and 59·50 per cent. of iron, numbers closely approaching those obtained by Lindström. The sp. gr. of the mineral was 4·12—4·2. J. R.

A New Niobium Mineral from Amhurst Co., Virginia. By Wm. Brown (*Chem. News*, xxxvi, 158).—The mineral occurs along with allanite.

Nb_2O_5,Ta_2O_5.	WO_3.	SnO_2.	ZnO_2.	Eb_2O_3,Y_2O_3.
48·66	0·16	0·08	2·09	27·94
(Ta_2O_5 about 2 p. c.)				(Y_2O_3 about 1 p. c.)

Ce_2O_3.	La_2O_3.	Di_2O_3.	UO.	MnO.	FeO.	BeO.	MgO.
1·37	3·92	4·06	3·47	trace	2·04	0·62	0·05

CaO.	Li_2O.	Na_2O.	K_2O.	F.	H_2O.	
2·61	trace	0·16	0·06	trace	3·19	= 100·48

M. M. P. M.

Native Antimony Ochre from Arkansas. By J. R. Santos (*Chem. News*, xxxvi, 167).—The ochre occurs in Sevier Co., accompanying stibnite. Hardness, a little over 4. Sp. gr. = 5·58.

Sb.	O.	H_2O.	Silica.
76·15	19·85	3·08	0·92

leading to the formula $2Sb_2O_4.H_2O$. The mineral is possibly a mixture of cervantite and stibiconite. M. M. P. M.

An unusual Form of Stibnite. By J. R. SANTOS (*Chem. News*, xxxvi, 167).—The specimen was from the Cabell mine in Grant co., Oregon: it was associated with red silver ore: it formed small globular masses, $\frac{1}{4}$ to $\frac{1}{2}$ inch diameter, often presenting a thin exterior shell of quartz with crystalline outer surface. When broken across, the nodules showed a fibrous structure. M. M. P. M.

Auriferous Cobalt from Grant Co., Oregon. By ST. G. BRYAN (*Chem. News*, xxxvi, 167).

S.	As.	Bi.	Co.	Ni.	Fe.	Cu.	Au.	As_2O_5.
3·23	49·19	1·31	11·19	3·79	12·82	2·44	trace	2·30

Cl.	CoO.	MgO.	Na_2O.	K_2O.	SiO_2.	H_2O.
trace	trace	0·94	0·30	0·40	9·71	1·52 = 99·14

Hence the approximate constitution—

Smalltite (ferriferous)	76·88
Chalcopyrite	7·09
Arsenates (erythrite, &c.)	5·46
Quartz	9·71

The gold was present to the extent of 6 oz. per ton.
M. M. P. M.

Aluminous Chrysocolla from Utah. By J. R. SANTOS (*Chem. News*, 167).—Colour, light greenish-blue; streak pale-blue; subtranslucent; hardness not much over 2.

SiO_2.	Al_2O_3.	CuO.	H_2O.
37·19	10·78	26·03	25·76

Hence the formula, $CuSiO_3.2H_2O$, where one-half the copper is replaced by an equivalent amount of aluminium. M. M. P. M.

An Ancient Specimen of Tin. By A. H. CHURCH (*Chem. News*, xxix 167).—A strip of metal taken from the heart of a mummy of about the date 600 or 700 B.C., was found—by sp. gr. method—to be almost perfectly pure tin. M. M. P. M.

Nickeliferous Iron from St. Catherine in Brazil. By M. GUIGNET (*Compt. rend.*, lxxxiv, 1507—1509).—In a letter from M. Guignet to M. Daubrée, he says that the so-called nickeliferous iron of St. Catherine, which is now exhausted, was in reality a meteorite weighing about 25,000 kilograms, the last portions raised being poor in nickel and cobalt. M. Daubrée adds a few observations on some of the chemical changes produced by atmospheric action on the surface of meteorites, and concludes by pointing out that in all probability the St. Catherine meteorite did not fall alone, and that it would be interesting to search for what he calls its satellites. J. M. T.

Galena, from Engelskirchen. By GURLT (*Jahrb. f. Min.*, 1877, 300).—The galena of this district occurs drusy, in the combination $\infty O \infty . O$; often in penetration-twin cubes, which are rare with galena. Sometimes massive galena is found enclosing quartz crystals well developed at each end, which occurrence closely resembles the quartz of quartz-porphyry, seldom being observed in veins. The quartz crystals must either have been formed before the galena or simultaneously with it. C. A. B.

Heubachite, a Natural Hydrated Oxide of Cobalt and Nickel. By F. SANDBERGER (*Jahrb. f. Min.*, 1877, 299—300).—Found in extremely thin soot-like deposits, or more rarely in dendritic foil and fine globular aggregations on clefts in barytes, at the St. Anton Mine in the Heubachthal, near Wittichen. Colour deep-black, streak exhibits a semi-metallic lustre, H = 2·5. Spec. gr. 3·44.

It is infusible before the blow-pipe, but dissolves in hydrochloric acid with evolution of much chlorine, the solution having a deep bluish-green colour, but changing into rose-red on dilution with water. Chemical composition as follows:—

CoO.	NiO.	Fe_2O_3.	MnO_2.	H_2O.
65·50	14·50	5·13	1·50	12·59 = 99·22

Heubachite is therefore a pure hydrated oxide. It is a very recent formation, being found only on clefts in barytes, and cementing together fragments of quartz and felspar, which have arisen from the disintegration of the neighbouring vein-rocks and been carried by the action of water into the barytes clefts. This water no doubt contained the constituents of heubachite in solution in the form of carbonates. Heubachite is found occurring under exactly similar circumstances at the Eberhard mine near Alpirsbach in the Schwabian Schwarzwald.
C. A. B.

Glaucodote. By W. J. LEWIS (*Jahrb. f. Min.*, 1877, 300—301).—Glaucodote, or cobalt-arsenical-pyrites, is found at Hakausbö in large twin crystals, whose form fully coincides with the akontite of Breithaupt. The forms observed were ∞P, $\infty P\bar{\infty}$, $P\bar{\infty}$, $\frac{1}{2}P\breve{\infty}$, $P\breve{\infty}$, $2P\breve{\infty}$, $P.P\bar{2}$. Twins according to two laws, the first being "the twin-plane a face of ∞P;" the second "the twin-plane a face of $P\bar{\infty}$. As the angle between two faces of this form is 61° 3′, a trilling can grow having a hexagonal appearance. A trilling of this mineral is to be seen at the British Museum. C. A. B.

A Lead Antimonite from Arnsberg, Westphalia. By F. PISANI (*Jahrb. f. Min.*, 1877, 300).—This mineral was found accompanying antimonite in steel-grey particles and in small acicular, strongly striated crystals in hollows in the antimonite. The crystal system of these crystals could not be determined. H = 2·5, spec. gr. = 5·5—95·73. Fuses before the blowpipe, evolving antimony fumes. Dissolves easily in hydrochloric acid. Chemical composition as follows, viz.:—

S.	Sb.	Pb.	Zn.
19·90	31·20	47·86	0·60 = 99·56

The author assigns to this substance the formula $7PbS.4Sb_2S_3$, and believes it to be feather-ore or heteromorphite. C. A. B.

The Colour of Zircon. By G. SPEZIA (*Jahrb. f. Min.*, 1877, 303—305).—The author heated some reddish zircons from Ceylon until they became colourless, and then hung them up by platinum wires in the same gas flame, some being in the reducing flame, others in the oxidising flame. After 25 minutes' heating no change was observed in the crystals hanging in the reducing flame, but those exposed to the oxidising flame were reddish, though not quite so red as previously. The red crystals were now reversed in the different flames, when the crystals which were coloured became colourless, and the colourless ones became red. A large crystal was similarly heated, when it was noticed that the change in colour took place from the exterior to the interior. Three colourless crystals were heated in a tube in a stream of oxygen, and three other colourless ones were heated in a tube drawn out to a fine point at one end (in order to exclude the air), when the three first mentioned crystals became red and the three last-mentioned remained colourless.

Other experiments were made, but all tended to prove that the ferric oxide present in zircon crystals is reduced to ferrous oxide when the crystals are colourless or green; whilst in the reddish crystals it exists unaltered as Fe_2O_3. The light-red crystals become darker in colour and cloudy on being exposed for a long time to the heat of the sun, but recover their original colour on being kept some time in a dark place. C. A. B.

Rutile, from the Binnenthal, after Specular Iron (Iron-glance). By G. VOM RATH (*Jahrb. f. Min.*, 1877, 297—298).—This occurrence is remarkable for the entire absence of specular iron and the contour of the original crystal being formed of rutile prisms. The original specular iron crystal exhibited the combination 0R, $\frac{4}{3}$P2. The rutile crystals exhibit the forms P.P∞, ∞P, ∞P∞, and some eight-sided prisms, amongst them being ∞P2. These crystals have three different positions, their vertical axes being parallel to the diagonals of the hexagonal plane 0R, and a face of ∞P∞ also being parallel and coinciding with the face of 0R of the original specular-iron crystal. Looking vertically upon the plane 0R, it is observed that the faces ∞P∞ of the rutile crystals are lustrous, and in three positions as already described; whilst the position of the pyramidal faces ($\frac{4}{3}$P2) are given by the refracted reflex of the faces of the primary pyramid of the rutile individuals occurring in two positions (that is, parallel to two of the diagonals of 0R), or by faces of ∞P2 of the rutile crystals having a position parallel to the third diagonal of OR. The parallelism of the rutile faces with the form of the original iron-glance, and the extent to which the hexagonal form of the latter was imitated by the rutile crystal-groups, was proved by goniometrical measurements. There can be no doubt that this remarkable occurrence is a pseudomorph of rutile after iron-glance.

Octlings of Rutile from Arkansas.—In this twin formation the terminal edge angle of $P\infty$ can be repeated eight times round a certain point in one plane: it becomes therefore possible for the faces of eight individual crystals to come in contact parallel to a terminal edge of $P\infty$, the vertical axes of these individuals running in a zig-zag direction up and down and almost enclosing the circle. The polysynthetical crystals of Magnet Cove are enclosed only by the form $\infty P2$, four faces of each individual occurring; but sometimes six faces of this prism occur on each individual, when it is observed that at each pole of the crystal-group there are funnel-shaped depressions. The author states that these twins of a new symmetry are formed in reference to an edge of a rutile pyramid, having an angle of 45°. A similar effort towards a higher symmetry is observed in rhombic trillings with a prismatic angle of 120°, and quadralings of felspar according to the Baveno law (twin-plane a face of $2P\infty$), in consequence of the edges of $2P\infty$ nearly approaching 90°. C. A. B.

The Crystal-form of the Strontianite of Hamm, Westphalia. By H. LASPEYRES (*Jahrb. f. Min.*, 1877, 294—295).—The strontianite of this locality occurs in veins and masses enclosed in limestone or a kind of marl in the chalk formation. The veins are constituted as follows: 1st, clay next to the "salbands;" 2nd, calcite; 3rd, strontianite in the interior, also enclosing a few drusy cavities. In the latter the finest crystals are found. The measurements made by Laspeyres furnished the following axial relations on calculation, viz.: $a : b : c = 0{\cdot}60920 : 1 : 0{\cdot}72431$ $\infty P - \infty P = 117° 18'$, $2P\breve{\infty} - \infty P\breve{\infty} = 145° 22' 45''$. Some forms entirely new to strontianite were observed, viz.: $\frac{1}{3}P$, $12P$, $40P$, $\frac{2}{3}P\breve{\infty}$ and $24P\breve{\infty}$. On most of the complicated crystals from Hamm $\infty P\breve{\infty}$ and ∞P occur prominently; all other forms are more secondary, thus, in the following order, P, $2P$, $2P\breve{\infty}$ and $4P\breve{\infty}$; then follow $12P$, $24P\breve{\infty}$, $12P\breve{\infty}$, $3P$, $40P$, $P\breve{\infty}$ and OP. There are four distinct types observed, viz.: (1) an acute acicular type through the predominance of the pyramids and brachydomes; (2) a tabular type through $\infty P\breve{\infty}$, with it occurring ∞P, $2P\breve{\infty}$; (3) a prismatic type with ∞P, $\infty P\bar{\infty}$, $\frac{1}{3}P$, $\frac{2}{3}P\breve{\infty}$; (4) a pyramidal type through the pyramids. Simple crystals are not found occurring in any of the four types, but always twins according to the law, "the twin plane a face of ∞P." These twins consist of beautiful "penetration twins," "contact twins," trillings, quadralings and polysynthetical twins. The acute pyramids and brachydomes are horizontally striated, but most particularly ∞P and $\infty P\breve{\infty}$. A curious occurrence of small regularly grown strontianite crystals is observed on the terminal faces of the larger crystals, such as P, $2P$ or $2P\breve{\infty}$.

The author is of opinion that this growth is not an after formation, but rather a partial continued development of the older crystal, as the small parasitical crystals are not only parallel to each other, but also to the older crystal, and are often influenced by the lamellar structure of the latter.

Laspeyres states that such instances are rare of a crystal building itself up in the direction of the vertical axis out of parallel-lying sub-individuals. C. A. B.

Polydymite, a New Mineral. By H. LASPEYRES (*Jahrb. f. Min.*, 1877, 296—297).—This mineral crystallises in the regular system in octohedrons which are polysynthetically twinned, the twin plane being a face of the octohedron. Most of the crystals are very tabular, through the predominance of the face parallel to the twin plane, and there are also prismatically developed octohedrons. Cleavage incompletely cubical. Fracture uneven to conchoïdal. H = 4—5. Sp. gr. 4·808—4·816. Somewhat sectile. Colour on freshly broken surfaces light steel-grey, becoming very soon dark-grey or yellow. Decrepitates before the blowpipe, fuses on charcoal to a blackish-green magnetic bead. Dissolves in nitric acid with separation of sulphur; does not dissolve in hydrochloric acid, but enclosed bismuth-glance is dissolved out by this acid. Strong metallic lustre. Chemical composition as follows, viz.:—

Ni.	Co.	Fe.	S.	As.	Sb.	
53·508	0·606	3·844	40·270	1·041	0·508	= 99·777

From this analysis the general formula, R_4S_5, is deduced. Polydymite is found in veins of other ores in Sayn-Altenkirchen, accompanied by millerite, bismuth-glance, zinc-blende, gersdorffite, ullmannite, lying on a layer of spathic iron and quartz. The author observed on one specimen that the crystals had lost their metallic lustre, and were converted into a reddish-brown substance. On breaking some of these pseudomorphs, it was observed that they were penetrated by fresh acicular millerite. From a careful examination of these crystals, Laspeyres is certain that the polydymite and millerite were simultaneously formed. C. A. B.

Saynite is not a Distinct Mineral, but a Mineral Mixture. By H. LASPEYRES (*Jahrb f. Min.*, 1877, 297).—This so-called mineral is known to occur only at the Grünau mine in the Sayn-Altenkirchen district, and was supposed to be a nickel-bismuth-glance crystallising in very small octohedrons or occurring in granular aggregations. The author dissolved out the bismuth-glance with hydrochloric acid, and on analysing the residue, found it to have exactly the percentage composition of polydymite. The granular impure variety of polydymite contained a greater amount of bismuth-glance than the crystallised polydymite, and coincided with the percentage composition of saynite: hence Laspeyres concludes that the latter is only a mixture of polydymite with bismuth-glance. C. A. B.

Some Minerals acompanying the Graphite of Mugrau, Bohemia. By A. SCHRAUF (*Jahrb. f. Min.*, 1877, 250—257).—The graphite of this district occurs in long layers enclosed in gneiss, and in immediate contact with limestone. The formation is enclosed in the district bounded on the east by Plaben and Krumau, and on the west by Winterberg, with a N.W.N. "strike," and an inclination of from 30° to 80°. Most of the graphite from this locality is of good quality. The gneiss appears to be considerably decomposed in the immediate neighbourhood of the graphite vein, being in some cases richer in iron, and occasionally passing into graphite-gneiss, the rock being thoroughly impregnated with it, and of a black colour. The following minerals accompany the graphite, occurring at the contact-zone of the graphite and calcite.

I. *Ihleite, a new mineral*, is amorphous, occurring either globular or reniform, exhibiting in section a confused reticulated structure, composed of fine lamellæ and fibres, which, however, on microscopical examination, do not appear to be crystalline. Soluble in cold water, but on warming it to 40° a basic ferric sulphate separates out. An analysis of samples of this mineral furnished the following results, proving the constancy of the process of formation, viz.:—

	1875.		1876.
SO_3	38·2	37·4	37·2
FeO......	2·1	26·1	1·4
Fe_2O_3	24·5		25·6
Al_2O_3		0·3	
CaO	—	0·4	0·3
H_2O......	35·5	35·6	35·3
	100·3	99·8	99·8

This substance appears, therefore, to be a combination of ferrous and ferric sulphates, with the formula $FeSO_4 + 9(Fe_2S_3O_{12}) + 120H_2O$. The mineral which most nearly approaches ihleite in composition is misy, which differs, however, from it in its absolute lower percentage of water and relative proportion of sulphuric acid, sp. gr. 1·812. Ihleite is of course a secondary product, formed by the oxidation of iron-pyrites, the largest and best specimens being always found in the impure, hard, stony graphite.

II. *Chloropal, from Mugrau*, occurs as a secondary product at the point of contact between the graphite and the rock enclosing it, the matrix of the chloropal being pure, lenticular, foliated graphite. Sulphur-yellow chloropal sometimes covers the graphite with a layer from 1 to 2 mm. in thickness, and thin layers of it are also found between the laminæ of graphite. In some cases very minute particles of graphite are enclosed in chloropal. At the contact surface with the graphite the chloropal possesses a lemon-yellow colour and weak lustre, whilst in the interior it has an earthy fracture and a lighter colour. Chloropal is very hygroscopic; it is, therefore, absolutely necessary to dry the specimens carefully in air previously to analysing it, otherwise the percentages of water obtained will vary considerably.

The author ascertained that a sample thoroughly dried in air furnished 18·32 per cent. of water; another sample dried over sulphuric acid 13·59 per cent.; and a third sample exposed to damp air, 22·02 per cent. It is therefore probable that this property of chloropal accounts for the variations in the amounts of water (10—26 per cent.) found by other authors. An analysis of two different samples gave the following results, viz.:—

	H_2O.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Alkalies.	SiO_2.	
No. 1..	19·62	27·50	4·16	2·97	1·77	traces	43·98	= 100·00
No. 2..	18·32	28·91	3·19	3·35	2·84	„	42·93	= 99·54

The formula derived from these analyses is $Ca_2Mg_2Al_2Fe_{14}Si_{28}O_{84} + 40H_2O$.

III. *Calcite* occurs in this locality either in narrow drusy hollows in pure graphite, or enclosed in reddish, weathered, amorphous quartz (as after formation). In both cases the calcite occurs in well-developed, acute, scalenohedrons, without secondary faces. The forms observed were R^9, R^{13}, and R^{15}, sometimes two of them being combined. R^{13} is very rare. C. A. B.

A Chalcedony-amygdaloïd filled with Water. By G. VOM RATH (*Jahrb. f Min.*, 1877, 302).—This specimen came from Brazil, and has a flat almond shape, is 45 mm. in length, 35 mm. in breadth, and 15 mm. in thickness. The chalcedony is deposited in concentric layers or shells, the inside of the shell being smooth and the exterior rough. The shell is filled three-fourths of its capacity with water, which it encloses, and which can be heard to splash against the sides of the shell upon moving it about. In one place the shell is only about 1 mm. in thickness. C. A. B.

The Rhombic Crystals of Sulphur obtained by Fusion. By G. VOM RATH (*Jahrb. f. Min.*, 1877, 302).—These crystals exhibit the combination P.P∞. Brame pointed out long ago (*Journal f. prakt. Chem.*, 55, 106) that fused sulphur could crystallise in the rhombic system. This statement is, however, doubted, but it may be stated that Silvestris described some rhombic crystals of sulphur, which were formed during the fire in the Floristella mine (*Pogg. Ann. Ergäng*, Bd. vi, 356). C. A. B.

The Crystallographical Constants of Lanarkite. By A. SCHRAUF (*Jahrb. f. Min.*, 1877, 298—299).—The author was enabled to determine the axial ratios of this mineral with great accuracy, and found it to crystallise in the monosymmetrical system, $a : b : c = 0·868113 : 1 : 1·383634$; $\eta = 91° 49'$. The commonest forms observed were 0P, ∞Ᵽ∞. — $\frac{1}{3}$Ᵽ∞, 3Ᵽ3 — 2Ᵽ10. Most complete cleavage parallel to 0P, the cleavage-faces possessing a splendid adamantine lustre. The orthopinacoïd predominates, but 3Ᵽ3 very often occurs; in fact the morphological character of lanarkite can easily be ascertained through the pyramidal faces. The domatic development of lanarkite, with its pyramidal terminations, causes it to resemble closely crystals of linarite and azurite. C. A. B.

Analysis and Fertilising Power of Lavas, &c. By R. Gavazzi (*Ann. Chim. Phys.* [5], xi, 244—255).—Lavas are divided into two distinct classes—(1.) Normal pyroxenic rocks, attacked by acids, and resembling basalt; (2.) Normal trachytic rocks, not attacked by acids, and resembling trachytes. The former contain about 48 per cent. of silica, the latter about 76 per cent.

The normal pyroxenic rocks consist of augite or hornblende, mixed with labradorite or anorthite; whilst the trachytic rocks generally consist of orthoclase and oligoclase mixed with a large quantity of silica.

The lavas, containing 48 and 75 per cent. of silica respectively, are to be considered as the extremities of the groups, and those intermediate as mixtures of these two in different proportions.

Other bodies, such as volcanic bombs, slag, sand, ashes, volcanic sandstone, and conglomerate, possess compositions similar to that of lava, and may be considered as different forms of that substance.

From the chemical composition sufficient reasons are found to explain the great fertilisation of land by lava, &c., emitted from volcanoes. L. T. O'S.

Analysis of the Mineral Waters of Neudorf, near Petschau, in Bohemia. By W. Gintl (*Wien. Akad. Ber.*, lxxv, 419—430).—The waters of two of the three springs were examined, the analyses of which show that they are very similar to those of the Victor's Spring at Königswarth, and Rudolf's Spa at Sangerberg. No. 1, most to the south, rises through a stratum of serpentine rock, as a clear stream, without colour or smell, but with a pleasant acid taste. It has an acid reaction, and gives off carbonic acid on warming, becoming alkaline. No. 2, most to the north, is slightly turbid, and gives off a large quantity of carbonic acid as it issues from the spring, but otherwise has similar properties to No. 1.

Parts per 1,000,000.

	No. I.	No. II.
Temperature	7·2° C.	8·0° C.
Specific gravity	1·00068	1·00073
Silicic acid	61·81	69·76
Potassium sulphate	9·75	11·23
Sodium ,,	4·46	·24
,, chloride	1·72	1·89
,, carbonate	3·64	15·44
Calcium ,,	24·39	69·22
Magnesium ,,	179·65	327·45
Manganous ,,	4·36	6·46
Ferrous ,,	8·63	3·71
Calcium phosphate	1·49	1·25
Ferric oxide	—	4·66
Free carbonic acid	1554·86	1193·78
Half combined carbonic acid	111·29	212·27
Free carbonic acid by volume	8646·7 c.c.	6662·4 c.c.

	No. I.	No. II.
Total solids	299·94	511·37
Alumina, strontium, lithium, ammonium, free oxygen, and nitrogen .	trace	trace

The above are represented as neutral carbonates. T. C.

Organic Chemistry.

Equivalents of Organic Compounds. By M. BERTHELOT *Compt. rend.*, lxxxiv, 1472).—In consequence of M. Wurtz affirming in a recent discussion that no reaction in organic chemistry gave rise to the formation of $HO = 9$, the author calls attention to a series of reactions to prove the contrary. He commences by saying that there are multitudes of reactions which result in the formation of this amount of water, but that they belong to that class which the supporters of atomic notation commenced by ignoring, and have now completely forgotten. For instance the determination of the equivalent of acetic acid; all chemists regard this as = 60. Various methods are used for its determination.

(1.) By determining the weight of acetic acid capable of producing one equivalent (say, 1 gram) of hydrogen in dissolving a metal.

$C_4H_4O_4 + Zn = C_4H_3ZnO_4 + H$, which the author regards as precisely similar to that of the univalent mineral acids.

(2.) By determining the weight of acetic acid capable of liberating 1 equivalent of water = 9 grams, by acting on the oxides of the metals such as—

$C_4H_4O_4 + AgO = C_4H_3AgO_4 + HO$. If, on the contrary, the molecular weight of acetic acid is taken as that liberating a molecule of water, $H_2O_2 = 18$, then the molecular weight of acetic acid would necessarily be 120.

$(\text{Ȼ}_2H_4\Theta_2)_2 + Ag_2\Theta = (\text{Ȼ}_2H_3Ag\Theta_2)_2 + H_2\Theta$. He thinks this to be a logical consequence of atomic notation; and adds "It may be seen from these that in organic as well as inorganic chemistry, $HO = 9$, $H = 1$, and $C_4H_4O_4 = 60$, represent three corelative weights." He argues that the same demonstration can be made for alcohol, $C_4H_6O_2$, and ethylene C_4H_4, so far as they are capable of disengaging 1 gram H by the action of K, or of combining directly with an equivalent weight of $HCl = 36·5$, and that these demonstrations based on direct combination, or equivalent substitution, may be applied to all organic bodies. J. M. T.

Fixation of Nitrogen on Organic Substances under the Influence of Feeble Electric Tensions. By M. BERTHELOT (*Compt. rend.*, lxxxv, 173—178). The author has found that the electric tensions at the poles of a battery (five Leclanché cells) can slowly induce the formation of ozone in an annular space between two glass tubes. The surfaces of the tubes external to the annular space, instead of having been provided with metallic coatings forming the poles of the battery, were severally in contact with dilute sulphuric acid into which the battery wires dipped.

A similar arrangement, but with tinfoil coatings replacing the sulphuric acid solutions, was used in experiments in which to the inner surface of one of the tubes bibulous paper was applied in two detached pieces, one moistened with water, and the other with a solution of dextrin. The poles of the battery were therefore separated by two thicknesses of glass and a space enclosing air and the moistened papers. At the end of a month, analysis showed that the paper moistened with water contained ·045 per cent. of nitrogen, while that moistened with the solution of dextrin contained ·192 per cent. Before the experiment, the papers contained respectively only ·010 and ·012 per cent.

The difference of electrical potential which was thus found capable of fixing nitrogen, is not greater than that frequently existing between strata of the atmosphere not far removed from the ground, and the author believes that his experiments indicate the true explanation of the fixation of nitrogen in nature. A calculation of the quantity of nitrogen which certain crops must derive from the atmosphere (apart from any ammoniacal salts existing there), leads to figures of the same order of magnitude as those given by the experiments. These results suggest new lines of physical, chemical, and physiological enquiry. R. R.

Reply to the Remarks of E. Chevreul respecting the Phosphorescence of Organic Bodies. By R. RADZISZEWSKI (*Compt. rend.*, lxxxiv, 656—657).—Although many organic substances absorb atmospheric oxygen, and oxidise rapidly in alkaline solution, it would appear that the more slowly the oxidation or alteration takes place under these circumstances, the more likely is the body to be phosphorescent.

Thus tannic, gallic, and pyrogallic acids, which oxidise very quickly in alkaline solution, are not phosphorescent.

Again, hydrofurfuramide, and the ordinary aldehydes, which are eminently unstable, are negative in their action, while their stable isomerides, furfurine and the polymerised aldehydes, are phosphorescent.

Of the thirty active organic bodies which the author has studied, lophine phosphoresces the most brilliantly. This substance withstands the action of strong alcoholic potash for a very long time, and is perhaps the best example that can be brought forward in support of the assertion which the author is desirous of maintaining, namely, that the phenomena of phosphorescence, as exhibited by organic substances, are in some way intimately associated with the slowness with which they undergo decomposition in alkaline solution. J. W.

Boron Fluoride as a Dehydrating Agent in Organic Chemistry. By F. LANDOLPH (*Compt. rend.*, lxxxv).—The author proposes this body as a dehydrating agent for organic chemistry. The following are abstracts of his results with certain bodies:—

Camphor.—This substance, powdered and gently heated, absorbs large quantities, forming a crystalline compound, having a melting point much lower than that of ordinary camphor. On distillation, this substance gives off large quantities of white vapours, having an acid reaction; and the distillation must be repeated to free the camphor entirely from the fluoride. In order to produce perfect dehydration, the substances must be heated in closed vessels to 250° for 24 hours. Under these conditions, the camphor disappears, with formation of boric acid, a liquid product consisting of cymene volatile at a temperature of 180°, and a solid substance volatile at about 350°.

Anethol.—The essence of green Russian aniseed absorbs large quantities of the fluoride at the ordinary temperature. The product seems to consist of two portions; the one distilling at 120 to 250°, the other below 350°. After washing with water, a liquid is isolated at 157 to 163°, no doubt a hydrocarbon, $C_{10}H_{16}$, corresponding with campholic aldehyde, which the author obtained by the oxidation of anethol.

Benzoic aldehyde.—This aldehyde combines directly with boron fluoride, forming a crystalline substance, which decomposes in the air, reproducing the aldehyde, together with boric and hydrofluoric acids. On heating the substances together in a closed vessel, a black, hard mass is obtained, yielding by extraction with ether a crystalline substance, which melts at 123—124°, and can be recrystallised from hot water. Fluoride of boron transforms chloral rapidly into metachloral. Glacial acetic acid gives very little anhydrous acid. Ethylene forms with the fluoride a liquid of agreeable odour, boiling at 125—127°, and burns with a green flame. It is violently decomposed by water, with formation of ethylene. J. M. T.

New general Method for the Synthesis of Hydrocarbons, Ketones, &c. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, lxxxiv, 1450—1454).—In continuation of their former communication, the authors here state that the reaction therein described takes place also when, for the derivatives of the alcohols of the fatty series, those of the aromatic series are substituted. Thus, benzyl chloride acts on benzene in presence of aluminium chloride, producing benzylphenyl, or diphenylmethane, a substance having a pleasant odour of fruit, and boiling at 260°. The reaction occurs also with chlorides containing more than one atom of chlorine. Thus, from tetrachloride of carbon, the authors obtained a new substance, *tetraphenylmethane*, as shown by the equation:—

$$CCl_4 + 4C_6H_6 = 4HCl + C(C_6H_5)_4.$$

This body boils at a temperature above the boiling point of mercury, and crystallises from alcohol in clinorhombic prisms. Oxygenated chlorides, such as those of the acid radicles, behave in a manner perfectly analogous to those before named.

From these facts it appears that the chlorine of alcoholic and of acid chlorides is easily replaced by hydrocarbon radicles, and especially by phenyl. This is not, however, the case, under the same conditions, with chlorine combined with phenyl: for chorinated benzene may be heated with a mixture of benzene and aluminium chloride without any extrication of hydrochloric acid. The authors attempted to obtain directly acids or ethers, by acting with aluminium chloride on a mixture of benzene and chloroxycarbonic ether; but carbonic acid gas, and not hydrochloric acid, was given off in this case, and the product contained no organic acid. R. R.

Experiments on Etherification. By N. Menschutkin (*Deut. Chem. Ges. Ber.*, x, 1728—1735).—This paper contains some results of the author's experiments on the rate of etherification of various alcohols by acetic acid. The experiments consisted in heating glass tubes of about 1 c.c. capacity, containing mixtures of alcohol and acetic acid in molecular proportions, in a bath of glycerin maintained at the temperature of 153—154°. The amount of ether thus formed in a given time was estimated by withdrawing a tube from the bath, cooling it quickly, and determining the residual acetic acid by titration with baryta-water.

The author estimated in this way the amount of ether formed in 1, 2, 4, 7, 10, 14, 24, 36, 42, 48, 72, 96, 120, and in a few cases 144 and 168 hours. The results are all given in a table accompanying the paper. The most important data are—(1). The initial rate of etherification (that is, the proportion of ether formed in the first hour, expressed in percentage of the total theoretical amount), and (2), the limit of etherification, similarly expressed. These numbers are given in the following table, which is an abstract of the author's:

	Initial rate.	Limit.
Methyl acetate	57·25	71·45
Ethyl ,, ...	46·60	69·61
Propyl	46·39	70·90
Isobutyl	45·40	73·46
Octyl	46·56	82·24
Cetyl	—	87·17
Allyl	36·80	61·88
Benzyl	37·77	63·97
Styryl	37·21	64·58

The author distinguishes between the absolute and the relative rate of etherification, meaning by the former the proportion of alcohol or acid actually etherified to the total quantity employed, and by the latter the proportion of ether formed to the amount determined by the limit of etherification. As regards the primary saturated alcohols, he points out that methyl alcohol differs considerably in its initial rate (absolute, 57·25; relative, 80·1) from the rest, which all have an absolute initial rate of about 46·5. A review of the whole of the numbers furnished by these alcohols (with the exception of methyl) shows that, though the rate of etherification during the first hour is nearly the same in all, it afterwards becomes distinctly greater in alcohols of higher molecular weight: hence the limit is also higher, as is shown by the table.

As regards the relative rate of etherification, it is shown that this decreases regularly with increase of molecular weight, the numbers for ethyl, propyl, isobutyl, and octyl alcohols being respectively 67·94, 65·43, 61·80, and 56·61.

In the non-saturated alcohols the initial rates, which are nearly the same in all, are about 10 lower than in the saturated alcohols. The relative rates for allyl, benzyl, and styryl alcohols are 59·46, 59·04, and 57·61 respectively.

The limit of etherification of the saturated primary alcohols (omitting methyl alcohol) increases with the molecular weight, being about two greater for each higher homologue, as is shown by the foregoing table. The author concludes, therefore, that differences in molecular weight have a much greater influence upon the limit of etherification than was thought by Berthelot and Péan de St. Gilles. J. R.

On the Normal Paraffins.—Part II. By C. S. Schorlemmer (*Phil. Trans.*, i, 1878, 1).—In the first paper of this subject it was shown that by the action of chlorine on a normal paraffin a primary chloride and a secondary one of the general formula $\left.\begin{matrix}C_nH_{2n+1}\\CH_3\end{matrix}\right\}CHCl$ are formed simultaneously (*Phil. Trans.*, vol. 162, part i, p. 111). It appeared of interest also to examine the action of bromine on the paraffins. The present paper contains the first results of this research.

I. *Normal Hexane.*—When bromine vapour is passed into the vapour of the boiling hydrocarbon, in daylight, its colour disappears quickly, and substitution-products are formed which are partly decomposed by distillation. The portion distilling without decomposition consists of a hexyl bromide, which was converted into the acetate and the alcohol. The latter yielded on oxidation *acetic acid* and *normal butyric acid*, showing that it is *methylbutyl carbinol.* The boiling points of the different compounds are as follows:—

	Formula.	Boiling point.
Bromide……	$\begin{matrix}C_4H_9\\CH_3\end{matrix}\ CHBr$	143—145°
Acetate	$\begin{matrix}C_4H_9\\CH_3\end{matrix}\ CH.OC_2H_3O$	146—150°
Alcohol	$\begin{matrix}C_4H_9\\CH_3\end{matrix}\ CH.OH$	136—140°

II. *Normal Heptane* yielded the following products:—

Bromide……	$\begin{matrix}C_5H_{11}\\CH_3\end{matrix}\ CHBr$	165—167°
Acetate	$\begin{matrix}C_5H_{11}\\CH_3\end{matrix}\ CH.OC_2H_3O$	169—171°
Alcohol……	$\begin{matrix}C_5H_{11}\\CH_3\end{matrix}\ CH.OH$	155—157°

The heptyl alcohol is *methylpentyl carbinol,* because on oxidation it was resolved into *acetic acid* and *normal pentylic acid.*

As result of this investigation, it appears that by the action of bromine on normal paraffins only secondary bromides of the general formula $\left.\begin{matrix}C_nH_{2n+1}\\CH_3\end{matrix}\right\}CHBr$ are formed, but not a trace of a primary bromide, or that the methyl groups which are present in these hydrocarbons, and which are readily attacked by chlorine, are not touched by bromine at all.

In addition to the secondary bromides, other products are formed which, on distillation, either decompose completely or are resolved into hydrobromic acid and non-saturated hydrocarbons, which are probably olefines. C. S.

Action of Sulphur at High Temperatures on Normal Paraffins. By S. CABOT (*Chem. News*, xxxvi, 114).—From an experiment undertaken by the author with the view of obtaining a sulphur-compound of the normal paraffins, which might be converted by oxide of lead into an oxide, and perhaps be of use in candle making, it was found that sulphur at high temperatures decomposes heptane, but that the products consist merely of sulphuretted hydrogen and free carbon. As this is most probably the case with all the other members of the group, the author does not think it worth while to attempt the formation of a sulphur-compound of the heavier and solid paraffins. D. B.

A New Hydrocarbon obtained from the Highest Boiling Portions of American Petroleum. By HEMILIAN (*Chem. Centr.*, 1877, 2).—This hydrocarbon, called *petrocene*, crystallises from boiling benzene in shining yellow laminæ, is almost insoluble in alcohol and ether, melts above 300°, and sublimes when carefully heated. Dilute nitric acid and chromic acid act as oxidising agents, forming a brown powder insoluble in the known solvents. This powder sublimes with decomposition. Concentrated nitric acid forms nitro-derivatives; bromine evolves hydrobromic acid; concentrated sulphuric acid forms a dark blue solution. The barium and lead salts of the sulpho-acid formed are completely insoluble in water. Since crystalline salts have not been obtained with this hydrocarbon, the author cannot safely consider it a homogeneous chemical compound. D. B.

Brominated Derivatives of Hexane. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 1234).—Hexane heated to 130—140° with bromine yields the compound C_6Br_8, together with another crystalline body $C_6Br_8H_4$. At 120—125° the latter is the chief product, accompanied, however, by two other bodies, $C_6Br_8H_6$ and $C_6Br_6H_8$.

The following bromine-derivatives of hexane have now been obtained:—$C_6Br_6H_8$, $C_6Br_8H_6$, $C_6Br_8H_4$, C_6Br_8, C_6Br_6 (see a former paper, *Deut. Chem. Ges. Ber.*, x, 402). J. R.

Derivatives of Ethylvinyl. By M. NEVOLÉ (*Compt. rend.*, lxxxv, 514).—Pure ethylvinyl acetate,* boiling at 110·5—111° (sp.

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* Lieben (*Bull. Soc. Chim.*, xii, 282) obtained this same body by transformation

gr. 0·896 at 0°), was converted into the corresponding alcohol by heating with more than the requisite quantity of strong potash in sealed tubes for ten hours at 130—135°. On distillation the greater part came over below 100°. After washing and drying this alcohol, a secondary butylic alcohol forms, a colourless mobile liquid, whose odour resembles that of fermentation butylic alcohol. It boils at 98·5—99°; its sp. gr. is 0·834 at 0°, and 0·818 at 21°.

Preparation of the Glycolbutylenic Derivative of Ethylvinyl.—About 300 grams of a mixture of 2 parts of vinyl bromide and 1 part of zinc-ethyl were heated in sealed tubes for five or six weeks. The gas formed was passed into bromine, and the product distilled. Two of the principal portions passed over at 160—166°, and at 182—184°. The portion boiling below 160° contained ethene bromide, and that boiling above 180° contained monobromethene dibromide. The liquid boiling at 160—166° was fractionated, and the portion boiling at 164—165° analysed. It contained 75·1 per cent. bromine (theory for ethylvinyl bromide 74·07 per cent.).

The portion boiling at 163—166° was heated with silver acetate and acetic acid in sealed tubes. The resulting liquid, freed from silver by baryta, and from baryta by carbonic acid, was purified by fractional distillation; it then formed a thick colourless liquid, of sweet taste, boiling at 192—193°. Analysis showed it to be butyleneglycol (mixed with some ordinary glycol). It is identical with that described by Grabowski and Saytzeff (*Liebig's Annalen*, clxxix, 325), which was prepared from normal primary butyl alcohol, by transforming this latter into iodide, and the iodide into butylene, which was combined with bromine. The bromide thus formed boiled at 164—165°, and furnished a glycol boiling at 191—192°.

The author concludes from these facts that the constitution of the butylene (ethylvinyl) formed by the action of zinc-ethyl on vinylbromide is $CH_3—CH_2—CH=CH_2$. C. W. W.

Preparation of Acetylene. By M. BERTHELOT (*Ann. Chim. Phys.* [5], x, 365—369).—Acetylene was prepared by the action of a red heat on ethylene or its derivatives, alcohol, ether, &c., and it was found that by this process ether gives the best yield. Sawitch proposed some years ago to obtain acetylene by shaking up ethylene bromide with an alcoholic solution of potash. This method, however, is to be less recommended even than the above. The action of an electric spark on hydrocarbons, if continued sufficiently long, is the process which gives the best yield of acetylene. The author recommends the preparation of this compound by means of the incomplete combustion of compound hydrocarbons, as coal gas (*Ann. Chim. Phys.* [3], lxvii, 52; [4], ix, 419), and by using the apparatus he proposes, a drawing of which is given, it is easy to collect the acetylene formed, while the apparatus once arranged, the action proceeds day and night, requiring little or no attention. T. C.

of secondary butylic iodide, prepared by the action of HI on C_4H_9ClO. It boils at 111°, and has a sp. gr. of 0·892 at 0°. The corresponding alcohol boils at 99° under 738 mm., sp. gr. 0·827 at 0°, 0·81 at 22°.

Action of Silver Cyanide on Dibromethyl Bromide. By A. ORLOWSKI (*Chem. Centr.*, 1877, 3).—$C_2H_3Br_3$, b. p. 185—186°, prepared, according to Tawildaroff, from $C_2H_4Br_2$, yields with silver cyanide the compound $C_2H_3(CN)_3(AgCN)_3$, in the form of yellow laminæ, soluble in alcohol. The ethereal solution deposits silver cyanide with decomposition, and the strained liquor yields, after removal of the ether, a thick mass solidifying over sulphuric acid.

D. B.

On Two New Ferricyanides and a Thiocyanoplatinate of Potassium. By G. WYROUBOFF (*Ann. Chim. Phys.* [5], x, 409—519).—1. *Ferricyanide of lead and potassium*, $(Cy_6Fe_2)Pb_2K_2.3H_2O$, crystallises in large hexagonal tables of a very dark red colour, transparent only when viewed in thin laminæ. It is very soluble in water, and is precipitated from its aqueous solution by alcohol. The crystals are decomposed on exposure to the air; the aqueous solution is likewise unstable in the air.

The relations of the axes in the crystals are $a : b : c = 1·7205 : 1 : 0·9309$. The salt sometimes crystallises in right rhomboïdal prisms.

2. *Ferricyanide of cadmium and ammonium*, $(Cy_6Fe)_2Cd_3.3(NH_4)_2O$, crystallises in red prisms, which on exposure to the air for some days lose ammonia, and are converted into a yellow crystalline powder, made up of minute rhomboïdal plates, having the composition $(Cy_6Fe)_2Cd_32(NH_4)_2O$. The crystals of the original salt are in the form of oblique rhomboïdal prisms, having an angle 63° 26′. The relations of the axes are $a : b : c = 0·6160 : 1 : 1·2425$; $\alpha = 85° 22′$.

3. *Potassium thiocyanoplatinate*, $(CyS)_6Pt.K_2.2H_2O$, crystallises in monoclinic prisms having an angle of 114° 25′, the relation of the axes being $a : b : c = 1·566 : 1 : 1·534$; $\alpha = 80° 46′$. The composition of the salt shows it to be closely related to the anhydrous salt, $(CyS)_6Pt.K_2$, prepared and described by Buckton (this *Journal*, vii, p. 22, 1854), from which, however, it differs in colour, and in not being permanent in the air.

C. F. C.

New Compounds of Thiocyanic Acid. By M. P. MIQUEL (*Ann. Chim. Phys.*, xi, 289—356).—*Thiocyanates of acid radicles* are prepared by the action of acid chlorides on dry lead thiocyanate. Neither mercuric, potassium, nor sodium thiocyanate can be used instead of the lead salt.

Acetyl thiocyanate is a pale yellow, strongly refracting liquid, possessing a penetrating odour, soluble in ether and carbon disulphide. It boils at 132—133°, undergoing partial decomposition, and its sp. gr. at 16° is 1·151.

It is decomposed by alkalis, acids, alcohol, and water, with formation of acetic and thiocyanic acids, &c.

Butyryl thiocyanate is a strongly refracting liquid boiling at 180°, and resembling the acetyl in its properties. The action of the aromatic acid chlorides on lead thiocyanate does not give rise to thiocyanates, as might have been expected, but to thiocarbimides. No satisfactory explanation can be given of this fact.

Benzoyl-thiocarbimide, $C_7H_5O.CS.N$, is a strongly refracting yellow liquid smelling of bitter almonds. Its sp. gr. at 16° is 1·197; at 200°

it decomposes, giving off torrents of carbon oxysulphide. This liquid dissolves in ether, carbon disulphide, and chloroform, and it unites with alcohol, forming an ether. By boiling water it is completely converted into benzamide and carbonyl sulphide, showing that the benzoyl thiocarbimide is free from the isomeric compound benzoyl thiocyanate. The thiocarbimide polymerises, forming metabenzoyl thiocarbimide, a yellow amorphous powder melting at 160°.

Salicyl-thiocarbimide is a thick syrupy liquid. The compound obtained by Rathke and Schæfer (*Ann. Chem. Pharm.*, clxix, 101) by the action of thiocarbonyl chloride on amidobenzoic acid resembles metabenzoyl thiocarbimide in its chemical and physical properties. Miquel proposes to call it metasalicyl thiocarbimide, and to regard it as a polymeride of salicylic thiocarbimide. The thiocarbimides are deprived of their sulphur by the oxides of silver, lead, and mercury; at the same time they split up into carbon dioxide and a nitril, *e.g.*, $C_7H_5O.CS.N + Ag_2O = Ag_2S + C_7H_5N + CO_2$.

Ammonia converts the thiocarbimides into thiocarbamides (sulphureas), but it decomposes the acid radicle thiocyanates, *e.g.*, acetyl thiocyanate yields acetic and thiocyanic acids and perthiocyanogen.

The following thiocarbamides have been prepared by acting on benzoyl or salicyl thiocarbimide with ammonia or a monamine. Di- and triamines have no action on these compounds.

Benzoyl-thiocarbamide, $CSNHC_7H_5ONH_2$, also prepared by Pike (*Deut. Chem. Ges. Ber.*, iv, 755), forms small prismatic crystals, possessing a bitter taste, soluble in alcohol. It melts at 171°, and is converted into benzoyl urea by oxide of lead or mercury.

Salicyl-thiocarbamide resembles the preceding compound in its properties. It melts at 182°.

Benzoyl-ethyl-thiocarbamide, $CS\left\{\begin{matrix}NHC_7H_5O\\NHC_2H_5\end{matrix}\right.$, crystallises in colourless prisms soluble in alcohol, which melt at 134°. Mercuric oxide converts it into benzoyl-ethyl-carbamide, melting at 192°.

Acetyl-phenyl-thiocarbamide, $CS\left\{\begin{matrix}NHC_2H_3O\\NHC_6H_5\end{matrix}\right.$, obtained by the action of phenylamine on acetyl thiocyanate, crystallises in thin plates melting at 169—170°, soluble in alcohol and ether. It unites with hydrochloric and hydrobromic acids, *e.g.*, $HBr.CS(NH)_2C_7H_5O.C_6H_5$. This body forms large prisms, melting with decomposition at 270°. The crystals are very soluble in water, they are decomposed by ammonia with formation of the thiocarbamide.

Benzoyl-phenyl-thiocarbamide, $CS\left\{\begin{matrix}NHC_7H_5O\\NHC_6H_5\end{matrix}\right.$, forms long colourless flexible needles, insoluble in water and ether, melting at 148—149°. It does not unite with hydrobromic acid, but is converted into nitrobenzoyl-phenyl-thiocarbamide, $CS\left\{\begin{matrix}NHC_7H_6O.NO_2\\NHC_6H_5\end{matrix}\right.$, by the action of nitric acid. This nitro-product crystallises in silky needles melting at 230°, insoluble in the usual solvents.

Salicyl-phenyl-thiocarbamide has been prepared by Merz and Weith, and by Rathke and Schæfer. It is absolutely insoluble in water and melts at 191—192°.

Benzoyl-benzyl-thiocarbamide, $CS\left\{\begin{matrix}NHC_7H_5O\\ NH(C_6H_5,CH_2)\end{matrix}\right.$, forms small colourless prisms, melting at 145° to a liquid which solidifies without resuming its crystalline texture. An isomer, *benzoyl-paracresylthiocarbamide*, $CS\left\{\begin{matrix}NHC_7H_5O\\ NH(C_6H_4CH_3)\end{matrix}\right.$, is obtained by the action of toluidine on benzoyl-thiocarbimide. It crystallises in long brittle prisms melting at 165°, to a liquid which readily recrystallises.

Benzoyl-naphthyl-thiocarbamide, $CS\left\{\begin{matrix}NHC_7H_5O\\ NHC_{10}H_7\end{matrix}\right.$, is insoluble in water and ether. It forms yellow tasteless prisms, melting at 172°. This compound is much more stable than the preceding thiocarbamide. Strong nitric acid partly decomposes it, but forms at the same time nitrobenzoyl-naphthyl-thiocarbamide, whilst treatment with mercuric oxide gives rise to a compound which is probably naphthyl-benzoyl-carbamide.

Action of Alcohols and Phenols on Thiocarbimides. Acetyl and butyryl thiocyanates dissolve in alcohol with simultaneous production of ethyl acetate or butyrate, thiocyanic acid, and some complex crystalline bodies. At the ordinary temperature, benzoyl-thiocarbimide combines with absolute alcohols or phenols to form ethers of thiocarbamic acid, *e.g.*, $\left.\left\{\begin{matrix}CS\\ C_7H_5O\end{matrix}\right\}N + C_2H_6O = CS\left\{\begin{matrix}NHC_7H_5O\\ OC_2H_5\end{matrix}\right.\right.$. Methyl and ethyl alcohol unite readily with the thiocarbimides, but the higher members of the series and the phenols require to remain in contact with the thiocarbimide several weeks or months before complete union is effected.

These ethers are easily decomposed by heat or by the action of acids or alkalis; they are desulphurised by the oxides of silver and mercury, forming the corresponding ethers of carbamic acid. An alcoholic solution of potash or soda forms with these thiocarbamates crystalline compounds identical with the potassium or sodium substitution-product obtained by the action of potassium or sodium methylate or ethylate on benzoyl-thiocarbimide.

Methyl-benzoyl-thiocarbamate is deposited from a boiling alcoholic solution in silky needles melting at 97°, decomposing at 105°. It is slightly soluble in water, and dissolves easily in ether and in methyl and ethyl alcohol. Its solution reduces silver, bismuth, and copper salts in the cold, and gives with mercuric chloride a white precipitate, and with gold chloride a yellow precipitate.

Sodium-benzoyl-thiocarbamate, $CS\left\{\begin{matrix}NNaC_7H_5O\\ OCH_3\end{matrix}\right.$, is obtained in small crystals by the action of alcoholic soda solution on the preceding compound, or by the action of sodium methylate on an ethereal solution of benzoyl-sulphocarbimide.

Ethyl-benzoyl-thiocarbamate is described by Loessner (*J. pr. Chem.*, [2], x, 235) as benzoyl-ethyl-oxythiocarbamic acid. It is a crystalline body, slightly soluble in water; it melts at 73—74°, and decomposes at 85°.

Amyl-benzoyl-thiocarbamate is a syrupy liquid. *Phenyl-benzoyl-thiocarbamate* is a slightly yellow crystalline body, insoluble in water, very soluble in alcohol and ether. It melts at 93°, and decomposes at a slightly higher temperature.

Inorganic thiocyanates. Silicon thiocyanate, prepared by the action of silicon tetrachloride on lead thiocyanate, melts at 142°, and boils at 300°. Its vapours burn in the air with a lilac flame; they are decomposed by passing through a red-hot tube. The thiocyanate is insoluble in the usual solvents; it dissolves in a mixture of benzoyl and thiocyanic acid, and on evaporation rectangular prisms are deposited. It is decomposed by moisture, forming thiocyanic acid and silica; with alcohol, ethyl silicate and thiocyanic acid are formed. The crystals impart a red stain to paper, cotton, the skin, and other organic bodies. (The red colour produced by adding an alkaline thiocyanate to an acid solution is often due to the presence of organic dust, and not to iron salts.)

Arsenious thiocyanate, $As(CNS)_3$, resembles the preceding compound in its properties and mode of preparation, but is much more difficult to isolate.

Phosphorus thiocyanate, $P(CNS)_3$, obtained by acting on a mixture of dry sand and lead thiocyanate with phosphorous chloride, is a liquid having a sp. gr. at 18° of 1·625, boiling at 260—270°, and decomposing at higher temperatures. It does not solidify at −20°. Its vapours burn with a brilliant flame; under certain conditions they are spontaneously inflammable. They produce violent headache, and are poisonous. This compound does not decompose on exposure to the air, and is only slowly attacked by water.

The thiocyanates of iodine, antimony, and tin have not been isolated. W. C. W.

The action of Monochloracetic Acid on Thiocyanic Acid, and its Salts. By M. NENCKI (*J. pr. Chem.* [2] xvi, 1—17).—When an aqueous solution of monochloracetic acid is heated with ammonium thiocyanate to 70°, a reaction takes place, hexagonal crystals being obtained on cooling the mixture. The substance thus formed, which has been called *rhodanic acid,* is but slightly soluble in cold water, but is dissolved with ease by alcohol or ether, and has the constitution $C_3H_3NS_2O$. With metallic salts, especially those which have a greater affinity for sulphur than for oxygen, crystalline precipitates are formed. Copper rhodanate $(C_3H_2NS_2O)_2Cu + H_2O$, when suspended in water and treated with hydrochloric acid, dissolves, recrystallising in yellow needles of the composition $(C_3H_3NS_2O)_2CuCl$. The reaction between chloracetic acid and ammonium thiocyanate probably takes place according to the following equation:—

$$2(CNS.NH_4) + C_2H_3ClO_2 + H_2O = C_3H_3NS_2O + 3NH_3 + CO_2 + HCl,$$

but at the same time hydrocyanic acid, sulphuretted hydrogen, and carbon oxysulphide are produced.

Rhodanic acid dyes. When one part of rhodanic acid dissolved in boiling water is added to a concentrated solution of five parts of ferric chloride, a brown precipitate is at first produced, which soon changes to brown-red, gas being disengaged at the same time. This brown powder (rhodan-red) having the constitution $C_9N_3H_5O_3$, acquires a metallic green colour when rubbed in the dry state. It dissolves easily with red colour in caustic alkalis, and appears to play the part both of a base and of an acid. A secondary product appears also to be formed at the same time as rhodan-red; this body is insoluble in cold alcohol, and forms a violet solution with ammonia; it appears to consist of hydrogen, carbon, and sulphur only. Both the red and the violet colours can be "fixed" on silk or wool.

Carbaminthiacetic acid. This substance, produced by the action of thiocyanic acid on chloracetic acid, is soluble in water and alcohol; has the constitution $NH_2.COS.CH_2.COOH$; melts at 143°, and is, therefore, not identical with Heintz's thiocyanacetic acid, which melts at 128°; moreover, when heated it yields thioglycollic acid. No metallic salts of this acid have been obtained, for the cold aqueous solution decomposes into cyanic and thioglycollic acids.

E. W. P.

Action of Monochloracetic Acid on the Thiocyanates of the Aromatic Monamines. By J. H. JÄGER (*J. pr. Chem.* [2], xvi, 17—29).—Following up Nencki's research on the action of chloracetic acid on the thiocyanates, the author caused monochloracetic acid to react with aniline thiocyanate, the result being analogous to that obtained when aniline acts on ammonium thiocyanate. Ammonium thiocyanate and chloracetic acid were added to an alcoholic solution of aniline, and the whole heated; the crystals which were formed on cooling appeared, when washed with water, to be non-homogeneous: it was found excessively difficult to separate the two sets of crystals, but the separation was finally accomplished by dissolving out the one set by ether. The substance thus obtained was easily soluble in water, reacted acid, and formed neither salts nor an acetyl substitution-product; it was oxidised by nitric acid to a yellow amorphous mass, and had the formula $C_9H_{10}N_2SO_2$. The reaction had therefore taken place as follows:—

$$C_6H_5NH_2 + CSNH + CH_2ClCOOH = C_9H_{10}N_2SO_2 + HCl.$$

Paratoluidine, under the like circumstances, yielded a substance consisting of $C_{10}H_{12}N_2SO_2$. The crystals melted at 176—182°, at which temperature they appeared to decompose, the aniline compound melted at 148—152°. At a higher temperature, acetic acid vapours were given off. In fact the two compounds were analogous in all their properties. If then in the above reactions the aniline produces with chloracetic acid, phenylglycocine ($C_6H_5.NH.CH_2.COOH$) which, combining with thiocyanic acid, forms phenyl glycocine-thiocarbamide, then by the action of alkalis or acids, phenylglycocine and thioxycarbamic acid should be formed according to the equation:—

$$NH_2.CS.C_6H_5N.CH_2CO_2H + H_2O = C_6H_5{-}NH.CH_2.CO_2H + NH_2.CS.OH.$$

Such is not found to be the case, but monophenylcarbamide ($C_7H_8N_2O$) is produced, together with thioglycollic acid.

The tolyl-product in like manner breaks up, under the action of acids, into tolyl-carbamide and thioglycollic acid. E. W. P.

Direct Conversion of Nitrils into Compound Ethers. By H. BACKUNTS and R. OTTO (*Chem. Centr.*, 1877, 5).

—By allowing hydrochloric acid gas to act on a solution of the nitrils in absolute alcohol, they are readily converted into compound ethers. This conversion takes place more easily by means of sulphuric acid. The authors have in this manner prepared ethyl acetate from acetonitril, ethyl propionate from propionitril, and ethyl benzoate from benzonitril.

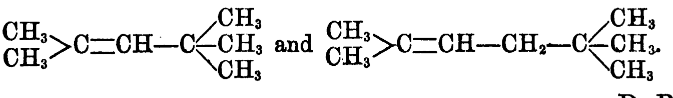
D. B.

A Peculiar Decomposition of Boric Ether. By HUGO SCHIFF (*Liebig's Annalen*, clxxxix, 162—165).

—A sample of ethyl borate which had lain for two years in a stoppered vessel having a very narrow communication with the outer air, was found to contain a glassy transparent solid. This solid the author believes to be H_3BO_3, but he has not completely examined its nature. M. M. P. M.

Action of Dilute Sulphuric Acid on Trimethyl Carbinol. By A. BUTTLEROW (*Chem. Centr.*, 1877, 2).

—By warming this mixture to 100°, diisobutylene was obtained, forming a colourless readily mobile liquid, having a boiling point of 102·5°, and a slight smell of petroleum. Its hydriodide yields with oxide of silver an octyl alcohol, boiling at 146·5—147·5°, similar in smell to camphor, and retaining water with great obstinacy (a difficultly decomposible hydrate is probably formed), the alcohol solidifying at 20° to a white crystalline mass. When oxidised with chromic and metaphosphoric acids, the hydrocarbon and the alcohol yield identical products—carbonic acid, acetone, trimethylacetic and acetic acids, an acid of the formula $C_8H_{16}O_2$, and a ketone-like body, $C_7H_{14}O$. From these data the author gives to diisobutylene and diamylene the following structural formulæ :—



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}CH{-}C{<}\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix} \text{ and } \begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}CH{-}CH_2{-}C{<}\begin{matrix}CH_3\\CH_3.\\CH_3\end{matrix}$$

D. B.

Preparation of Allyl Iodide and Acetic Anhydride. By J. KANONNIKOFF and MICHAEL SAYTZEFF (*Liebig's Annalen*, clxxxv, 191).

—The authors prepare allyl iodide as follows :—Iodine (1,000 grams) and highly concentrated glycerin (3,000 grams) are introduced into a large tubulated retort connected with a tubulated receiver. The tubulure of the retort is placed in connection with a carbonic acid apparatus, and that of the receiver with the chimney. When all the air has been swept out of the apparatus, from 300 to 600 grams of phosphorus are introduced in small portions into the retort. The first portions usually react violently, but afterwards the action becomes less energetic, and it is sometimes necessary to aid it by gentle heating. After all the phosphorus has been introduced, the mixture is distilled until it begins to froth violently, by which time the greater part of the allyl iodide has passed over; that remaining in the retort is distilled off with steam. In this way 1,000 grams of iodine yielded 1,100—1,150 grams of allyl iodide.

Acetic anhydride is prepared by the authors by an adaptation of Linnemann's process for the preparation of butyric acid, namely, by heating acetyl chloride with glacial acetic acid in a retort with reversed condenser till hydrogen chloride is no longer evolved, and then fractionating, with the help of a dephlegmator. The yield is about 50 per cent. of the theoretical amount. J. R.

Note on the Preparation of Ethene Glycol by Hüfner and Zeller's Method. By H. GROSHEINTZ (*Bull. Soc. Chim.* [2], xxviii, 57).—The carbon dioxide set free in the preparation of glycol by this method is accompanied by a large proportion of monobromethene (C_2H_3Br), whereby the theoretical yield of glycol is considerably diminished. L. T. O'S.

Specific Rotatory Power of Cane-sugar. By B. TOLLENS (*Deut. Chem. Ges. Ber.*, x, 1405—1414).—The researches of Landolt (*Deut. Chem. Ges. Ber.*, vi, 1078), of Hesse (*Liebig's Annalen*, clxxvi, 89 and 189), and those of the author on the glucoses (*Deut. Chem. Ges. Ber.*, ix, 1538), show that the rotatory power is not a constant property of a substance, but varies within a certain limit according to the nature and amount of the solvent. Cane-sugar exhibits this property, and this paper contains an account of experiments made to determine this specific rotatory power, and how it varies with the concentration of the aqueous solution. The author finds that it diminishes with increasing concentration, and taking the percentages of sugar (P) as abscissæ, and the rotations as ordinates, he constructs a curve for which he gives the formulæ—

I. $P\ (\alpha)^D = 66{\cdot}8102 - 0{\cdot}01553\ P - 0{\cdot}000052462\ P^2$ $(\alpha)^D =$ the angle of rotation. P varies from 0 — 18.

II. $(\alpha)^D = 66{\cdot}386 + 0{\cdot}15035\ P - 0{\cdot}0003986\ P^2$, P varying from 18—69.

These formulæ are calculated for cases when the specific gravities are reduced to 4° C.; and in order to make them available in practice the author gives the following for cases when the specific gravities are determined at 17·5° C.:—

III. $(\alpha)^0 = 66{\cdot}7268 - 0{\cdot}015534\ P - 0{\cdot}000052396\ P^2$, P varying from 5—18.

IV. $(\alpha)^D = 66{\cdot}3031 + 0{\cdot}015016\ P - 0{\cdot}0003981\ P^2$, P varying from 18—69.

In formula II, when P = 100 the specific rotatory power of sugar in the solid state is 63·90°. The author points out that it would be advantageous if chemists took a conventional specific rotatory power, *e.g.*, that of a 10 per cent. solution, which according to formula I would be $(\alpha)^D$, 10 = 66·65°.

The author, in conclusion, draws attention to the researches made in this direction by Biot (*Memoire de l'Acad. de l'Institut*, xiii, 118), who determined the specific rotatory power of sugar, and found it 42·45°. In repeating these experiments the author finds that errors arise from the difficulty in reading exactly, and also from the formation of glucose.

In these experiments Wild's polaristrobometer was used.

P. P. B.

Specific Rotatory Power of Cane-sugar. By M. SCHMITZ (*Deut. Chem. Ges. Ber.*, x, 1414—1420).—This paper contains an account of experiments made with the same object as those of Tollens (*Deut. Chem. Ges. Ber.*, x, 1403). The author finds with Tollens that rotatory power of sugar diminishes with increasing concentration of the aqueous solution, and gives the following formula to calculate the specific rotatory power:—

$$[a] = 64{\cdot}156 + 0{\cdot}051596\,q - 0{\cdot}0002805\,q^2.$$

q = the percentage of water.

From this formula sugar has in the solid state the rotatory power 64·156° at 20°.

For ordinary use, the author gives the formula—

(1.) $[a]^D = 66{\cdot}453 - 0{\cdot}0012362\,c - 0{\cdot}000117037\,c^2$, c being the weight of sugar in 100 c.c. of water, and varying from 85·6895—10·3994 grams.

(2.) $[\alpha]^D = 66{\cdot}639 - 0{\cdot}0208195\,c \pm 0{\cdot}00034603\,c^2$, $c = 26{\cdot}048 - 16{\cdot}35$, and of special value for experiments with Soleil-Scheibler's or Soleil's original apparatus.

For cases where c varies between 27·6407—2·4995 the author gives the equation $[\alpha]^D = 66{\cdot}541 - 0{\cdot}00841532\,c$. The determinations were made with three different forms of polarising apparatus.

P. P. B.

Studies on Glycerin, Cellulose, and Gum. Change of Glycerin into Glucose. By C. KOSMANN (*Bull. Soc. Chim.* [2], xxvii, 246—250).—The chemical action produced by the oxidation of iron by air and water can be communicated to other bodies, and by this means the author has saponified hog's lard into the fatty acids and glycerin. The glycerin so formed is further oxidised, and condenses to form glucose. The reaction is expressed thus: $2C_3H_8O_3 + O_2 = C_6H_{12}O_6 + 2H_2O$. Pure glycerin yields the same result, and when it is oxidised by a solution of permanganate of potash exposed to sunlight, glucose is formed. If the solution be boiled, the glucose is resolved into aldehyde and formic acid, as follows: $C_6H_{12}O_6 = 2C_2H_4O + 2CH_2O_2$. Oxidation with potassium bichromate and sulphuric acid also yields glucose.

Cellulose treated with potassium permanganate, or potassium bichromate and acetic acid, yields glucose, dextrin, and formic acid. This reaction is expressed as follows: $2C_6H_{10}O_5 + 2H_2O + 6O = 6CH_2O_2 + C_6H_{12}O_6$.

Iron in contact with air and water reacts on cellulose to produce glucose and a gummy substance insoluble in alcohol, and converted into glucose by boiling with dilute sulphuric acid. The soluble ferment of foxglove converts cellulose into glucose and dextrin, as the author has shown it do with starch (this *Journal*, 1877, i, 488).

Gum arabic is converted into glucose by the ferment of foxglove, and by iron in contact with air and water into glucose and dextrin.

All the glucoses obtained yield alcohol on fermentation.

P. P. B.

Abstractor's Note.—Leo Liebermann (*Deut. Chem. Ges. Ber.*, x, 2045) points out, in a criticism on Kosmann's results, that the bodies supposed to be glucoses are solutions of a ferrous salt, or of ferrous oxide, in glycerin, or of a lower oxide of manganese in glycerin, and, in cases where chromic acid is used, a glycerin solution of chromic oxide. All these solutions reduce Fehling's solution. Further, he supposes that the observed fermentation of the glucoses is really the fermentation of glycerin, which is attended with the formation of gas bubbles and metacetonic acid. P. P. B.

Further Observations on Lactoglucose and Galactose, obtained by the Action of Dilute Sulphuric Acid on Lactose. By H. FUDAKOWSKI (*Chem. Centr.*, 1877, 6).—The following differences were noticed:—Melting points 70° and 115°. 1 mol. lactoglucose reduces 5 mols. cupric sulphate; 1 mol. galactose reduces only 4 mols. Galactose crystallises from alcohol (98 p. c.) without water of crystallisation. Lactoglucose yields gluconic and saccharic acids; gluconic acid again yields tartaric acid, while galactose gives pyromucic acid. D. B.

Action of Potassium Permanganate on a Neutral Solution of Dulcite. By H. FUDAKOWSKI (*Chem. Centr.*, 1877, 5).—A sugar was obtained, optically indifferent, and related by its reducing properties to the series of $C_6H_{12}O_6$. D. B.

Acetic and Butyric Ethers of Quercite. By L. PRUNIER (*Bull. Soc. Chim.* [2], xxviii, 64—67).—Quercite forms three ethers with butyric acid: monobutyrin, $C_6H_{10}O_4(C_4H_8O_2)$; tributyrin, $C_6H_6O_3(C_4H_8O_4)_3$; and pentabutyrin, $C_6H_2(C_4H_8O_3)_5$, which are prepared by heating quercite with the requisite quantity of ordinary butyric acid.

These three ethers resemble one another very closely in their physical properties; they are amorphous colourless solids, or syrups, slightly deliquescent, bitter, very soluble in ether, less soluble in alcohol, and sparingly in water, but more so in water containing free butyric acid.

The three acetins, prepared by heating quercite with glacial acetic acid, resemble the butyrins very closely. They are amorphous solids, having an exceedingly bitter taste.

These, as well as other similar ethers prepared by Berthelot, tend to show that quercite is a pentatomic alcohol. L. T. O'S.

Triethylamine Derivatives. By VICTOR MEYER (*Deut. Chem. Ges. Ber.*, x, 1291).—In continuation of his former remarks, the author now states that although benzyl iodide is evolved when crude triethylbenzyl ammonium iodide (prepared from triethylamine and benzyl chloride, then treated with silver hydrate, and subsequently with hydriodic acid) is distilled with strong hydriodic acid, this result is not brought about by the decomposition $N(C_2H_5)_3(C_7H_7)I + HI = C_7H_7I + N(C_2H_5)_3,HI$, but is due to the presence of impurities; no triethylamine is obtained from this residue on distillation with potash, unless the substance originally employed contained a triethylamine salt.

C. R. A. W.

Diacetonamine and Vinyldiacetonamine. By W. Heintz (*Liebig's Annalen*, clxxxix, 214—230).—The acid oxalate of diacetonamine may be readily prepared by acting on a weighed quantity of oxalic acid with acetone and alcohol: details are given in the original. When this oxalate is boiled with alcohol and acetone in proper proportions, the neutral oxalate of vinyldiacetonamine is obtained. The acid oxalate may also be produced by treating the neutral salt with oxalic acid. By decomposing the neutral oxalate with strong potash-ley, the free base is obtained as a thick colourless liquid, boiling at about 200°. Analysis leads to the formula $C_8H_{15}NO$ for this base. Vinyldiacetonamine is the same as the base formerly described (this *Journal*, 1876, ii, 382) as isotriacetonamine, to which the author assigned the formula $C_9H_{17}NO$: his later formula is believed by him to be the correct one.

Investigations show that commercial acetone contains a substance or substances the presence of which renders possible the formation of vinyldiacetonamine from such acetone. The author is engaged in attempting to discover what this substance is.

The *sulphate* crystallises in microscopic needles, easily soluble in water, sparingly in alcohol, insoluble in ethers. The crystals do not give off water at 105°, but decompose completely at a higher temperature.

M. M. P. M.

Action of Hydrocyanic Acid upon Diacetonamine Chloride. By W. Heintz (*Liebig's Annalen*, clxxxix, 231—240).—Hydrocyanic acid decomposes an aqueous solution of diacetonamine chloride at 120° with production of a body crystallising in rhombic prisms which are very easily decomposed; analysis led to the formula $C_7H_{15}N_2OCl$. On addition of platinic chloride hydrocyanic acid is evolved, and the platinum salt of diacetonamine is produced. The action of strong hydrochloric acid upon a mixture of diacetonamine in aqueous solution and hydrocyanic acid, previously maintained for some time at 120°, results in the production of a substance having the formula $C_7H_{13}NO_2$. This body crystallises in colourless prisms, melting above 180°. It appears to form no compound. For the two substances which he has obtained the author suggests the formulæ—

$$CH_3{-}C(OH.CN)CH_2{-}C(CH_3.CH_3.NH_2) \text{ and}$$
$$CH_3{-}C(O{-}C{=}O)CH_2{-}C(CH_3.CH_3.NH_2) \text{ respectively.}$$

M. M. P. M.

Ethylate of Chloral. By Ad. Wurtz (*Compt. rend.*, lxxxv, 53—54).—The boiling point of this substance is 116°; whereas that of the hydrate, according to the author, is lower. This would form an exception to the general rule were it not known that both the hydrate and the ethylate decompose when heated, and their vapours occupy four volumes. It is, moreover, shown by the author that crystallised potassium oxalate loses its water of crystallisation in the vapour of the alcoholate as easily as in air; whereas in the vapour of the hydrate it does not: this proves that the water exists as such in the vapour of chloral hydrate. W. R.

Glyoxylic Acid. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, x, 1243—1248).—The author has examined the action of hydrogen sulphide on glyoxylic acid and its silver salt, but appears to have arrived at no definite results. J. R.

Normal Caproic Acid, Normal Hexyl Alcohol, and Normal Œnanthylic Acid. By AD. LIEBEN and C. JANECEK (*Liebig's Annalen*, clxxxvii, 126—152).—Starting from normal butyric acid, Lieben and Rossi prepared and investigated normal butyic alcohol (*Chem. Soc. Jour.*, 1872, 516). From this alcohol, by conversion into cyanide and distillation with potassium hydrate, they prepared and investigated normal valeric acid (*Chem. Soc. Jour.*, 1872, 1043). Next, by the distillation of a mixture of valeral and formate of calcium, the acid was converted into the normal valeric aldehyde, which by the action of sodium-amalgam was transformed into normal amylic alcohol (*Chem. Soc. J.*, 1872, 1033). Lastly, this alcohol was converted, through the cyanide, into normal caproic acid (*ibid.*). By this means was obtained a solid basis for future investigation into the higher members of the series. Subsequently Lieben examined the caproic acid contained in fermentation butyric acid, and found it to be substantially identical in its properties with the synthetically prepared normal caproic acid (*Chem. Soc. Jour.*, 1874, 248). Lieben and Janecek now resume the subject.

Caproic acid. The acid obtained from fermentation butyric acid was carefully purified and compared with the synthetically formed normal caproic acid, and that obtained from the normal hexyl alcohol of Heracleum oil by Franchimont and Zincke (*Chem. Soc. Jour.*, 1872, 61). The acid boils at 204·6 to 205·6° at a pressure of 759 mm., and has a sp. gr. of 0·945, at 0°, of 0·9289 at 20°, and of 0·917 at 40°. The synthetically formed acid boils at 204·5 to 205° at a pressure of 738·5 mm., and has a sp. gr. of 0·9449, at 0°, of 0·9294 at 20°, and of 0·9172 at 40°, whilst that derived from Heracleum oil boils at 204·5 to 205° at a pressure of 761·2 mm. All these may therefore be supposed identical. Their derivatives confirm this.

Ethyl Caproate, $C_2H_5.C_6H_{13}O_2$, boils at 166·9 to 167·3° at a pressure of 738 mm., and has a sp. gr. of 0·8898 at 0°, of 0·8728 at 20°, and of 0·8596 at 40°. That obtained from the synthetical acid boils at 165·5 to 166° at a pressure of 735·8 mm., and has a sp. gr. of 0·8898 at 0°, of 0·8732 at 20°, and of 0·8594 at 40°; whilst that from Heracleum oil boils at from 164·9 to 165·9°, to from 166·5° to 167·5°, and has a sp. gr. of 0·8765 at 17·5°.

Calcium caproate, $Ca(C_6H_{11}O_2)_2 + H_2O$, is a crystalline salt of which water, at 12°, dissolves 2·36 per cent. of the anhydrous salt, according to the authors, though Kottal (*Chem. Soc. Jour.*, 1874, 249) found 2·75 per cent. dissolved at a temperature of 19·5°, and Grillone 4·4 per cent. at a temperature of 21—22°. The calcium salt from the synthetically prepared acid has the same formula, and water at a temperature of 18·5° dissolves 2·7 per cent. of the anhydrous salt.

Barium caproate, $Ba(C_6H_{11}O_2)_2$. At 11·5° water dissolves 12 per cent. of the anhydrous salt, though Grillone found at 22° it dissolved only 85 per cent., and at 18·5° only 8·49 per cent. of the salt derived from the synthetically prepared acid. Kottal obtained a salt crystallising with three molecules of water, and soluble in water at 23° to the extent of 11·52 per cent. of the anhydrous salt. The authors obtained, however, only a salt of the form $5Ba(C_6H_{11}O_2)_2 + 9H_2O$, which dissolved in water at 10·5° to the extent of 11·14 per cent. A similar salt is formed by the synthetically prepared acid.

Caproic aldehyde, $CO.C_5H_{11}.H$. Prepared by the dry distillation of 10 parts of calcium caproate and 7¼ parts of calcium formate, the calcium caproate yielding 45½ per cent. of crude aldehyde. When pure, caproic aldehyde forms a limpid colourless liquid with the characteristic aldehyde odour, boiling at 127·9° at a pressure of 737·6 mm., and having a sp. gr. of 0·8498 at 0°, of 0·8335 at 20°, and of 0·8208 at 40°. With sodium bisulphate it yields a white crystalline mass. It is readily oxidised, and as readily polymerised.

Caprone $CO(C_5H_{11})_2$. Found amongst the higher-boiling fractions of the crude aldehyde. After purification it forms a white crystalline body, melting at 14·6° and boiling at 226·3° at a pressure of 740 mm., whilst its sp. gr. at 20° is 0·8262, and at 40° 0·8159. Its vapour-density is 5·98.

E. Schmidt found caprone from a similar source to boil at 220—221°, and to have a sp. gr. of 0·822 at 20° (*Chem. Soc. Jour.*, 1872, 892). The caprone of Brazier and Gossleth (*ibid.*, 1850, 250) boiled at 165°, and must have been entirely dissimilar. Caprone is not acted on by sodium bisulphite solution; it forms substitution-products with bromine, and when oxidised with bichromate, decomposes very slowly, yielding principally valeric acid and carbonic anhydride, with traces of butyric acid.

Hexyl alcohol, $C_6H_{13}OH$, was obtained from the caproic aldehyde by the action of sodium-amalgam in the usual manner. It boils at 157·2° (bar. at 740·8 mm.), and has a sp. gr. of 0·8333 at 0°, of 0·8204 at 20°, and of 0·8107 at 40°. It is therefore identical with the hexyl alcohol obtained by Franchimont and Zincke from Heracleum oil, which boils at 156·6° (bar. 752·5 mm.) and has a sp. gr. of 0·819 at 23° (*Chem. Soc. Jour.*, 1872, 61).

Hexyl bromide, $C_6H_{13}Br$, was prepared by acting with gaseous hydrobromic acid on the alcohol, and heating in sealed tubes. It boils at 155·5° at a pressure of 743·8 mm., and has a sp. gr. of 1·1935 at 0°, of 1·1725 at 20°, and of 1·1561 at 40°.

Hexyl iodide, $C_6H_{13}I$, was prepared in a similar manner. It boils at 181·4° at a pressure of 746·8 mm., and has a sp. gr. of 1·4607 at 0°, of 1·4263 at 20°, and of 1·4178 at 40°; whilst the iodide derived from Heracleum oil boils at 179·5° at a pressure of 752·5 mm., and has a sp. gr. of 1·4115 at 17·5°.

Hexyl chloride boils at about 133°, and ethyl hexyl ether at about 134—137°.

Œnanthylic acid, $C_7H_{13}O_2.H$, was prepared by the conversion of normal hexyl alcohol into the cyanide, and thence by the action of potassium hydrate into the normal œnanthylic acid. When pure œnanthylic acid forms a colourless oily liquid with a fatty odour and very sour taste. On cooling it solidifies to a crystalline mass melting at −10°. It boils at 222·4° at a pressure of 743·4 mm., and has a sp. gr. of 0·935 at 0°, of 0·9198 at 20°, and of 0·9084 at 40°. Franchimont found that normal œnanthylic acid from Heracleum oil boiled between 223° and 224° at a pressure of 762·7 mm., melted probably at −10°, and had a sp. gr. of 0·9212 at 24° (*Chem. Soc. Jour.*, 1878, 55). Schorlemmer and Grimshaw found for normal œnanthylic acid from the œnanthol derived from castor oil, a boiling point of 223—224° at a pressure of 763 mm., a melting point of −10·5°, and a sp. gr. of 0·9346 at 0°, of 0·9279 at 8·5°, of 0·9217 at 16°, and of 0·9146 at 29° (*Chem. Soc. Jour.*, 1873, 1073). (These sp. gr. are reduced to the same datum as those used by the authors, when the sp. gr. of water at the same temperature as the substance is taken for unity.)

Ethyl œnanthylate, $C_2H_5.C_7H_{13}O_2$, was prepared by acting with sulphuric acid on an alcoholic solution of the acid. It is a limpid body, with an ethereal odour, boils at 189·3° under a pressure of 747·6 mm., and has a sp. gr. of 0·8879 at 0°, of 0·8716 at 20°, and of 0·8589 at 40°. For the ether prepared by Franchimont, the boiling point was 187—188° at a pressure of 761·1 mm., and the sp. gr. 0·874 at 24° ; whilst Schorlemmer and Grimshaw found the ether prepared by them to boil at 187—188° at a pressure of 763 mm. and to have a sp. gr. of 0·8735 at 16°.

Calcium œnanthylate, $Ca(C_7H_{13}O_2)_2 + H_2O$, is soluble in water at 11° to 13°, to an amount of from 0·9166 to 0·268 per cent. of the anhydrous salt. Schorlemmer and Grimshaw found that 100 grams of water at a temperature of 8·5° dissolved 0·9046 gram of the anhydrous salt.

Barium œnanthylate, $Ba(C_7H_{13}O_2)_2$, is soluble in water at a temperature of 8° to 10° to the extent of 1·6743 gram of anhydrous salt, the amount found by Schorlemmer and Grimshaw being 1·7 gram in 100 grams of water at 12°.

The authors therefore conclude: (i) that the caproic acid found in crude fermentation butyric acid is the normal acid, identical with that obtained by Lieben and Rossi by synthesis, and by Franchimont and Zincke from Heracleum oil; (ii) that the hexyl alcohol which is derived from this fermentation caproic acid, is identical with the normal hexyl alcohol obtained by Franchimont and Zincke from Heracleum oil; (iii) that the œnanthylic acid obtained primarily from this fermentation caproic acid is the normal acid, and identical with that obtained by Franchimont from Heracleum oil, and by Schorlemmer and Grimshaw from œnanthol derived from castor-oil. E. N.

Levulinic Acid. By A. VON GROTE and B. TOLLENS (*Deut. Chem. Ges. Ber.*, x, 1440—1441).—In order to ascertain the correctness of Conrad's statement (*Liebig's Annalen*, clxxxviii, 223), that levulinic acid and β-acetopropionic acid are identical, pure levulinic acid was prepared and its properties examined.

The pure acid forms deliquescent crystals melting at 32·5—33·5°, and boiling at 235—255°. Ethyl levulinate boils at 200—201° under 756 mm. pressure. β-acetopropionic acid also forms deliquescent crystals melting at 31° and boiling at 239°. Its ethylic ether boils at 203—205°.

The silver salts of both acids are difficultly soluble; their other salts are easily soluble. Copper levulinate forms dark-green needles; sodium levulinate resembles calcium lactate in appearance.

The only point of difference between the two acids is in the calcium salt. Calcium levulinate contains two molecules of water of crystallisation; calcium β-acetopropionate is anhydrous. To decide the question of the identity of these acids, the authors intend to study the products of decomposition of levulinic acid. This acid was formed in small quantities by the action of dilute sulphuric acid on grape sugar perfectly free from levulose. W. C. W.

Identity of Helm's Oxyheptylic Acid with Ley's Acid. By A. POPOFF and VASSILIEFF (*Chem. Centr.*, 1877, 3).—Both these acids are obtained from bromheptylic acid. Since, according to Ley, the hydroxyl group is nearest to the carboxyl group, the authors assume that in the bromination of heptylic acid at 100° (Ley), as well as at 140—160° (Helms and the authors), the bromine-atom enters into the molecule at the place nearest to the carboxyl group. D. B.

Sarcolactic Acid. By KLIMENKO (*Chem. Centr.*, 1877, 3).—Contrary to Wislicenus, the author does not obtain the difficultly crystallisable zinc salt of sarcolactic acid (easily soluble in alcohol) by decomposing ethylsarcolactate of zinc with alcohol; this fact confirms Erlenmeyer's statements. The author has, however, prepared this salt from ordinary lactate of zinc by means of alcohol. Its formation depends on an admixture of lactic anhydride (which yields non-crystalline salts), or on a deficiency of the corresponding quantity of water necessary to form a crystalline salt containing a certain quantity of water of crystallisation. D. B.

Synthesis of Diallyloxalic Acid. By MICHAEL SAYTZEFF (*Liebig's Annalen*, clxxxv, 183—191).—Metallic zinc, acting on a mixture of ethyl oxalate and allyl iodide, produces a compound which, when distilled with water, yields *ethylic diallyloxalate*:

$$(CO.OC_2H_5)_2 + 2Zn + 2C_3H_5I = C_2H_5O.CO—C(C_3H_5)_2O(ZnI) + C_2H_5.O(ZnI);$$

$$C_2H_5O.CO—C(C_3H_5)_2O(ZnI) + H_2O = C_2H_5O.CO—C(C_3H_5)_2OH + ZnI(OH).$$

Ethylic diallyoxalate is a colourless liquid of faint ethereal odour, boiling at 213·6°. Its sp. gr. is 0·9873 at 0°, and 0·9718 at 18°. When heated with caustic baryta, it is converted into barium diallyloxalate, from which the free acid is obtained by decomposition with sulphuric acid.

Diallyloxalic acid crystallises in radiated groups of needles, or in long bundles of microscopic rectangular crystals. It dissolves easily in alcohol and ether, sparingly in water; melts at 48·5°, and distils without decomposition.

The *barium salt*, $(C_8H_{11}O_3)_2Ba$, crystallises in delicate needles, which dissolve easily in water and alcohol.

The *zinc salt*, $(C_8H_{11}O_3)_2Zn + 1\frac{1}{2}H_2O$, formed by neutralising the acid with zinc carbonate, resembles the barium salt.

The *lead salt*, $(C_8H_{11}O_3)_2Pb + 2H_2O$, crystallises from concentrated solutions in stellate groups of monoclinic crystals. It melts at 100°, slowly giving off its water of crystallisation.

The calcium, ammonium, sodium, and silver salts have also been prepared. Solutions of the last turn brown, even in the dark and in a vacuum.

Tetrabromodiallyloxalic acid, $C_8H_{12}Br_4O_3$, is a crystalline substance, formed on mixing a cooled solution of diallyloxalic acid in ether with a slight excess of bromine. J. R.

Action of Bromine on Succinic Acid. By C. ORLOWSKI (*Chem. Centr.*, 1877, 4).—In the absence of water, mono- and dibromosuccinic acids are produced. By using aqueous succinic acid, an oil is obtained as a secondary product ($C_2H_3Br_3$ acc. to Carius), which the author recognises as a mixture, $C_2HBr_5 + C_2H_2Br_2 + CHBr_3 + C_2H_2Br_4$. D. B.

Sodium-potassium Citrate. By TH. PUSCH (*Arch. Pharm.* [3], xi, 47).—To prepare this salt, 100 parts of citric acid are dissolved in a quantity of distilled water, sufficient for solution, and treated with 108 parts of pure potassium carbonate. The mixture is filtered after addition of 221 parts of crystallised sodium carbonate, evaporated on a water-bath to a syrupy consistence, and left to crystallise. The prismatic crystals thus obtained are drained and dried on blotting-paper; and the mother-liquors are evaporated till they solidify on cooling to a crystalline crust. The latter may be used as powdered sodio-potassic citrate.

The author recommends the use of this compound in medicine, as all the other citrates analogous to the tartaric acid preparations are very unstable salts, whereas this double salt may be kept for any length of time without altering. D. B.

Ethenyltricarbonic Acid. By A. ORLOWSKI (*Chem. Centr.* 1877, 5).—Ethylic monobromosuccinate, a fragrant liquid, not boiling without decomposition, yields, when treated with potassium cyanide, an oily ether, $C_2H_3(CN)(CO_2C_2H_5)_2$. The free acid was separated by hydrochloric acid, and converted into the tricarbonic acid, $C_2H_3(CO_2H)_3$, by treatment with warm potash-lye. D. B.

Vegetable Acids of Wine. By H. BRUNNER (*Chem. Centr.*, 1877, 4).—The fact that Malic, succinic, glycollic, and oxalic acids, which are found in unripe grapes, together with tartaric acid, may either be formed by direct building up of the molecules in the plant, or their formation may be partly direct and partly indirect. The latter assumption seems to agree best with laboratory results, and the following series, starting from the hypothetical carbonic acid, CO_3H_2, may represent the gradual change of carbonic acid into other vegetable acids under the reducing influence of light:—

$$\underset{\text{Carbonic acid.}}{2CH_2O_3} + H_2 = \underset{\text{Oxalic acid.}}{C_2H_2O_4} + 2H_2O; \qquad 2C_2H_2O_3 + H_2 = \underset{\text{Tartaric acid.}}{C_4H_6O_6};$$

$$C_2H_2O_4 + H_2 = \underset{\text{Glyoxylic acid.}}{C_2H_2O_3} + H_2O; \qquad C_4H_6O_6 + H_2 = \underset{\text{Malic acid.}}{C_4H_6O_5} + H_2O;$$

$$C_2H_2O_3 + H_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3}; \qquad C_4H_6O_5 + H_2 = \underset{\text{Succinic acid.}}{C_4H_6O_4} + H_2O.$$

This series is supported by various chemical observations. It is known that formic and oxalic acids are the first reduction-products of carbonic acid. When other reducing agents, *e.g.*, hydrogen, act on oxalic acid in the form of ethyl oxalate, glyoxylic acid is first formed, and from this acid either glycollic, tartaric, or deoxalic acid is obtained, according to the number of molecules added to the molecule of hydrogen; thus:—

$$\underset{\text{Glyoxylic acid.}}{C_2H_2O_3} + H_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3}. \qquad 2C_2H_2O_3 + H_2 = \underset{\text{Tartaric acid.}}{C_4H_6O_6}.$$

$$3C_2H_2O_3 + H_2 = \underset{\text{Deoxalic acid.}}{C_6H_8O_9}.$$

The change of oxalic acid and glyoxylic acid by hydrogen is well known; the formation of tartaric acid from glyoxylic acid by the same reaction was demonstrated by Debus in 1873, and it is further known that tartaric acid is easily transformed by reducing agents into malic acid, thence into succinic acid. The author therefore believes that the same successive reactions go on in the plant; that malic and succinic acids contained in the grapes are derivatives of previously formed tartaric acid, and that the latter is produced, by the influence of light in the chlorophyll cells, from carbonic acid and water, glycollic, glyoxylic, and oxalic acids occurring as intermediate bodies. The juice of unripe grapes appears in fact to contain malic, glycollic, and succinic acids, in addition to tartaric; and in the juice of very young grapes, gathered just after the flowers had withered, the author and Brandenburg have found an acid exhibiting the characters of glyoxylic acid. The occurrence of succinic acid in grape-juice is in accordance with the fact that this acid is also found in wine. It is indeed erroneous to impute the total acidity of wine to tartaric acid, inasmuch as succinic acid is often present in much larger proportion.

D. B.

Acetylene-Urea. By HUGO SCHIFF (*Liebig's Annalen*), clxxxix, 157—160).—Glyoxal and urea react upon one another, producing a crystalline body $C_4H_6N_4O_2$. The author has obtained crystals, having slightly differing forms, according to the condition of experiment; he is not certain whether the crystalline bodies are identical or isomeric. Their formulæ may be respectively $CO(NH)_2CH—CH(NH)_2CO$, and $CO(NH.CH.NH)_2CO.(NH)_2CO$, or perhaps the substance has the formula $(CH)_2(NH)_4(CO)_2$. M. M. P. M.

Decomposition of Chlorobenzene at a Red Heat. By J. G. KRAMERS (*Liebig's Annalen*, clxxxix, 135—141).—The decomposition was effected in a glass tube. The products were diphenyl, parachlordiphenyl, dichlorodiphenyl, paradichlorodiphenyl, and diphenylbenzene. About one-half of the total product, deducting the tarry matter which remained on distillation, consisted of parachlorodiphenyl. M. M. P. M.

Preparation of Isobutylbenzene. By J. WREDEN and B. ZNATOVICZ (*Chem. Centr.*, 1877, 6).—The authors obtained a comparatively large yield of this body (about one-fifth of the theoretical quantity), by the action of sodium on a solution of bromobenzene and isobutyl iodide in benzene. Only a small yield is obtained by the methods of Riess, Aronheim, and Köhler; or by the action of sodium on an undiluted mixture of benzyl chloride with isopropyl iodide or benzyl bromide and isopropyl iodide dissolved in an equal volume of ether. Pure isobutylbenzene boils at 167°. D. B.

Research on the Aromatic Amines. By E. NOELTING and J. BOAS-BOASSON (*Bull. Soc. Chem.* [2], xxviii, 2—5).—The authors describe a new method for the purification of monomethylaniline.

Monomethylaniline mixed with a large quantity of aniline and dimethylaniline, is treated with nitrous acid, whereby the last two are converted respectively into diazobenzene and nitrosodimethylaniline, which are both soluble in water, whilst the monomethylaniline yields methylphenylnitrosamine, a yellow oil, which is insoluble in water and acids, and on reduction yields monomethyaniline.

This method may be used for the determination of monomethylaniline. After treating the substance with nitrous acid, it is extracted with ether, which dissolves the methylphenylnitrosamine; the extract is then dried, the ether evaporated, and the oily residue is then weighed.

Dimethylaniline gives no oil, but leaves a few yellow crystals.

L. T. O'S.

Preparation and New Reactions of Acetylphenylnitrosamine. By A. MÜLLER (*Chem. Centr.*, 1877, 223).—This body may be prepared by the action of potassium nitrite upon acetanilide dissolved in nitric acid. Acetylphenylnitrosamine is decomposed by aniline salts; with production of amidazobenzene and acetic acid; by naphthylamine hydrochloride, with production of diazobenzeneamidonaphtalene, $C_{16}H_{13}N_3$. M. M. P. M.

An Isomeride of Benzenyldiphenylamidine. By AUGUST BERNTHSEN (*Deut. Chem. Ges. Ber.*, x, 1235—1237).—The author has shown in a previous paper (*Liebig's Annalen*, clxxxiv, 321), that amidines of the formula, $R(NH_2)C{=}NR$, or $R(NHR)C{=}NH$, are formed by the action of primary bases on nitrils. He is now investigating the action of secondary and tertiary bases on nitrils.

A mixture of benzonitril and diphenylamine hydrochloride, when heated to 180—200° for some days, yields a base which crystallises in thick, brilliant tables or prisms, melting at 111·5—112°, and agreeing in composition with the formula, $C_{19}H_{16}N_2$. The formation of this body, which the author calls *benzenylisodiphenylamidine*, is represented by the equation—

$$C_6H_5{-}C{\equiv}N + HN(C_6H_5)_2 = (C_6H_5).N(C_6H_5)_2C{=}NH.$$

At higher temperatures the product is a different base, of neutral reaction, melting at 182—183°, crystallising in yellowish prisms or tables, and agreeing in composition with the formula, $C_{19}H_{13}N$. This body is being further examined. J. R.

Action of Nitric Acid on Carbanilide. By ANT. FLEISCHER and GEORGE NEMES (*Deut. Chem. Ges. Ber.*, x, 1295).—Fleischer has stated in former communications that by the action of nitric acid on thiocarbanilide, tetranitroazoxybenzene results. Having experienced much difficulty in obtaining the product pure in this way, the authors examined the action of nitric acid on carbanilide (diphenyl urea): instead of producing tetranitrazoxybenzene, this reaction gives rise to *tetranitrodiphenylurea*: for on treating the product of the action (crystallised from a mixture of nitric and acetic acids) with tin and hydrochloric acid, there are formed *diamidodiphenyl-urea*, $CO\left\{\begin{matrix}NH.C_6H_4\\NH.C_6H_4\end{matrix}\right\}(NH_2)_2$, and small quantities of phenylene-diamine, melting at 139°. The former was isolated as crystalline tin compound, $C_{13}H_{14}N_4O.2HCl.SnCl_2$; the latter crystallised as hydrochloride; from these compounds the free bases were prepared. The nascent hydrogen thus altogether removed from the tetranitro-compound, two NO_2 groups, converting the other two into NH_2 groups. C. R. A. W.

Carbodiphenylimide and Phenylparatolylcarbamide. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 1234).—Carbodiphenylimide is readily formed by boiling thiocarbanilide in absolute alcohol with mercuric oxide.

Phenylparatolylcarbamide, when heated to 180° with excess of aniline or paratoluidine, is almost completely converted into diphenyl- or ditolyl-carbamide. J. R.

Reactions of Dimethylaniline. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 1235).—This substance, when heated to 180° with perchloromethane, yields [illegible] *carbotetradimethylaniline*, $C[C_6H_4.N(CH_3)_2]_4$; and when heated to 230° with chloroform, a *methenyltridimethylaniline*, $CH[C_6H_4.N(CH_3)_2]_3$. J. R.

Action of Nascent Hydrogen upon Thiobenzamide. By AUG. BERNTHSEN (*Deut. Chem. Ges. Ber.*, x, 36—38).—The author finds that by the action of sodium amalgam upon thiobenzamide in alcoholic solution, thiobenzaldehyde is formed according to the equation: $C_6H_5.CS.NH_2 + H_2 = C_6H_5.CSH + NH_3$. If, on the other hand, the hydrogen be evolved from zinc and hydrochloric acid, the S-atom and not the N-atom is eliminated thus:—

$$C_6H_5.CSNH_2 + 2H_2 = C_6H_5.CH_2NH_2 + H_2S.$$

Intermediate products, containing both nitrogen and sulphur, are formed in certain cases: *e.g.*, in the reduction of phenylthiacetamide.

The author has obtained thiacetamide, $CH_3.CS.NH_2$, by the addition of H_2S to acetonitril in alcohol-ammoniacal solution; it crystallises in colourless monoclinic prisms which melt at 108°, and are freely soluble in water, alcohol, and ether. C. F. C.

Hydrobenzamide, Amarine, and Lophine. By B. RADZISZEWSKI (*Deut. Chem. Ges. Ber.*, x, 70—75).—Lophine prepared by the destructive distillation of hydrobenzamide, crystallises in fine white needles melting at 275°. Alcoholic potash very slowly attacks this body, forming ammonia and potassium benzoate. In presence of air, this act of decomposition is accompanied by an evolution of light, which is clearly visible at + 10° and increases with the temperature until it attains its maximum intensity at 65°. The luminosity ceases if the air is expelled from the vessel containing the lophine, either by boiling the solution, or by a current of hydrogen. A solution of lophine in glacial acetic acid does not become luminous on oxidation with potassium permanganate.

Hydrobenzamide gives a feeble evanescent light with alcoholic potash. Under similar treatment amarine gives a slightly weaker light than lophine; it forms at the same time ammonia and a crystalline base, melting at 204°. W. C. W.

The Aromatic Hydrazine-compounds. By E. FISCHER (*Deut. Chem. Ges. Ber.*, x, 1331—1338).—This paper forms the continuation of the researches of the author on the same subject (*Chem. Soc. Journ.*, 1876 i, 576, 713, 911; ii, 527). Phenylhydrazine is known to unite readily with acetaldehyde and benzaldehyde to form crystalline neutral bodies, and the author now finds it to form with furfurol a perfectly analogous compound having the constitution $C_6H_5.N_2H.C_5.H_4O$. This body consists of plates having a faint yellow colour, melting at 96°, readily soluble in ether and alcohol, but only sparingly in ligroin, and decomposed into furfurol and phenylhydrazine by boiling with acids. It is important as affording a new basis from which to study the constitution of the furfuramides.

A cold aqueous solution of phenylhydrazine is converted by a stream of cyanogen gas into dicyanophenylhydrazine, $C_6H_5N_2H_3.(CN)_2$, a nearly colourless crystalline body, readily soluble in alcohol, but not easily purified. On being heated to 160°, it darkens and melts to an oily body, from which treatment with ether and ligroïn separates a substance crystallising in long glittering plates. This compound appears to possess basic properties, and is readily soluble in water and dilute acids. It reduces Fehling's solution, and is completely decomposed by long boiling with hydrochloric acid. When phenylhydrazine is heated with sulphur, it is converted into a mixture of aniline and benzene, together with some secondary products. In presence of water, phenylhydrazine is converted by iodine into diazobenzimide and aniline. Heated to 80° with potassium pyrosulphate, phenylhydrazine yields potassium phenylhydrazinesulphonate, identical with that prepared from diazobenzene.

The author concludes with an examination of the light thrown by his researches on the constitution of the diazo-compounds. They give $C_6H_5—NH—NH_2$ for the constitution of phenylhydrazine. Diazobenzene can be converted through diazosulphonic and hydrazinesulphonic acids into phenylhydrazine, and phenylhydrazine through hydrazinesulphonic acid into diazobenzenesulphonic acid. Phenylhydrazine can be formed by reduction from diazoamidobenzene, and both diazobenzene and phenylhydrazine yield diazobenzimide. These reactions indicate, therefore, that the diazo-compounds contain the group $-N=N-$, not, as Strecker supposes, $N\equiv N=$. E. N.

Paranitro-orthosulphophenol. By K. STUCKENBERG (*Deut. Chem. Ges. Ber.*, x, 55—57).—By a comparative examination of the salts of the respective acids, the author establishes the identity of nitrophenolsulphonic acid, prepared by nitrating orthosulphophenol with the acid obtained by substituting an H-atom of paranitrophenol by the sulpho-radicle, and thus corroborates the results obtained by Post. C. F. C.

Formation of Rosolic Acid from Cresol and Phenol. By KARL ZULKOWSKY (*Deut. Chem. Ges. Ber.*, x, 1201).—A mixture of 2 mols. of cresol, 1 mol. of phenol, and 3 mols. of sulphuric acid heated to 120° with powdered arsenic acid, rapidly assumes a dark brown colour, and forms after some hours a thick mass, from which water separates a resinous body having all the properties of rosolic acid. Phenol alone under the same circumstances yields no appreciable quantity of the colouring matter.

This process is analogous to that by which rosaniline is prepared. The reaction is an important addition to Liebermann and Schwarzer's discovery of the production of rosolic acid from salicylic aldehyde and phenol (*Deut. Chem. Ges. Ber.*, ix, 800; abstract *Journ. Chem. Soc.*, 1876, ii, 414). J. R.

Constituents of Creosote from Beechwood Tar. By FERD. TIEMANN and BENNO MENDELSOHN (*Deut. Chem. Ges. Ber.*, x, 57—63).—The authors have examined the two chief constituents, creosol and phlorol, of this creosote, *i.e.*, of the fraction boiling about 220°, with the view to establish their structural relations.

Creosol was converted into monac[illegible]l-creosol, and the latter oxidised by agitation with a solution of [illegible]otassium permanganate in presence of acetic acid. After saponifying the aceto-acid thus obtained, the solution yielded vanillic acid. Creosol appears, therefore, to be parahydroxyl-metamethoxyl-toluene.

The authors also describe a new ethyl ether of vanillic acid, the compound $C_6H_3.OH.OCH_3.COO.C_2H_5$. It is a colourless mobile liquid, boiling at 291—293°, and solidifying at 40° to a crystalline mass.

Phlorol was converted into methyl-phlorol, and the latter oxidised by boiling with a solution of potassium permanganate. The product, which also contained dimethyl protocatechuic acid, yielded, after fusion with potassium hydrate, oxyphthalic acid. Phlorol must hence be regarded as an oxyxylene, $C_6H_3.(OH).(CH_3)_2$.

A phlorol was also obtained by dry distillation from the calcium salt of phloretic acid. The known relation of this latter to anisic acid compels the inference that the phlorol in question is an ethyl-phenol, and therefore isomeric with the compound previously considered.

C. F. C.

Resorcin.

By L. CALDERON (*Compt. rend.*, lxxxv, 149—152).—This paper describes certain thermochemical determinations, from which it appears that resorcin behaves with bases like a diatomic phenol, and that the two equivalents of base with which it may be successively combined do not enter into the combination on the same footing. The first equivalent of base produces a compound analogous to an alkaline phenate; the second acts in a manner resembling the action of alkalis on ordinary alcohol, mannite, or glycerin.

R. R.

Action of Oxalic Acid on Resorcin at High Temperatures.

By CLAUS and ANDREÆ (*Deut. Chem. Ges. Ber.*, x, 1305).—When one molecule of resorcin and two of dehydrated oxalic acid are heated together in a sealed tube to 200°, a dark brown, slightly viscid substance is produced, which when diluted with alcohol and thrown into cold water, causes a yellow flocculent precipitate to form, whilst the aqueous liquid contains a substance which turns a fine blue with alkalis or alkaline carbonates, soon becoming dirty brown. The precipitated substance, when purified by repeated solution in alcohol and addition of water, dissolves in alkalis with a red or yellow colour, the solution being strongly fluorescent, of a green shade. It is apparently $CO\left\{\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}\right\}O$, and when heated with zinc-dust it forms diphenyl-ketone, phenol, and benzene. The authors propose to call it *diresorcin-ketone*. With bromine it forms an eosin-like precipitate of high colouring power. This has not been obtained pure, being apparently a mixture of tri- and tetra-brominated diresorcin-ketone.

C. R. A. W.

Chrysolin, a New Yellow Dye derived from Resorcin.

By F. REVERDIN (*Chem.* N[illegible], xxxvi, 136).—This colouring matter is formed by the simultaneous action of phthalic acid and sulphuric acid upon benzyl-resorcin. The latter is very readily obtained either by causing benzyl chloride to act upon resorcin in presence of a small quantity of zinc-powder, or by heating an alkaline and alcoholic solution of resorcin with benzyl chloride, or lastly by heating to about 150° in the oil-bath a mixture of 1 molecule of resorcin and 2 molecules of benzyl chloride. The latter method is the most simple, and may be further modified by adding the benzyl chloride gradually to the melted resorcin. The product, after heating, is poured into water, boiled to expel the last traces of benzyl chloride, left to settle, and decanted. The compound thus obtained is a strongly-coloured oil, very thick, and insoluble in water, in which it sinks. It distils at a very high temperature, with partial decomposition. It dissolves in alcohol with a yellow colour. The solution has a decided green fluorescence. Benzylresorcin dissolves also, with a yellow colour, in benzene, chloroform, and ether.

Preparation of Chrysolin.—The following method has been practised for several months at the works of Monnet and Co., Geneva:—460 grams of sulphuric acid and 1 kilo. of phthalic acid are heated in a retort of enamelled cast iron in the oil-bath to 130—140°. The latter substance is transferred into phthalic anhydride. 1 kilo. of resorcin, 460 grams of sulphuric acid, and 1 kilo. of benzyl chloride are then introduced into the retort, and the whole is heated gently over the water-bath. When no more hydrochloric acid is evolved, the reaction is completed by heating for twelve hours in the oil-bath to 135—145°. It is then left to cool, the solid broken up and dissolved in dilute caustic soda at the boiling point. When the residue no longer diminishes, the solution is filtered and the acid colouring matter precipitated by means of hydrochloric acid, washed with cold water, dissolved in carbonate of soda enough to saturate the acid, and evaporated to dryness. The soda salt of benzylated fluorescein constitutes chrysolin. The latter forms a mass with green metallic reflections, but is red-brown when reduced to a powder. It is soluble in water and alkalis, its solutions being precipitated by acids in yellow flocks. It yields bromated, iodated, and nitro-derivatives, which are all beautiful colouring matters. It may be fixed directly upon silk and wool. The latter, however, is preferably mordanted in a beck of lead acetate and alum. Cotton is mordanted with sulphate of alumina and dyed at a hand heat. The shade of chrysolin approaches that of turmeric. It resists the action of light well. By replacing benzyl chloride with the chlorides, bromides, and iodides of the fatty series, yellow colouring matters may also be obtained. Methyl resorcin, prepared by heating under pressure the resorcinate of soda in alcoholic solution with methyl chloride, also yields a yellow colouring matter. D. B.

Note on Pyrogallol. By OSCAR LOEW (*J. pr. Chem.* [2], xv, 322—327).—A dilute solution of pyrogallol, on gradually oxidising in presence of sodium phosphate, yields a crystalline body difficultly soluble in water or alcohol, but rather more soluble in ether and chloroform, and apparently consisting of pyrogallol-[illegible]none—$C_6.(C_6H_5O_3)_2H_4.O_2$. With acetate of lead it yields a precipitate consisting of a mixture of $C_{18}H_{10}Pb_2O_8$ and $C_{18}H_{12}PbO_8$. A concentrated solution of pyrogallol absorbs cyanogen, forming a cyanide which decomposes readily on heating. E. N.

Action of Bromine upon Phloroglucin. By R. BENEDIKT (*Liebig's Annalen*, clxxxix, 165—170).—By the action of 10 parts of bromine upon 1 part of phloroglucin, a solid substance is produced, which the author calls *phlorobromin*, C_6H_9BrO. It forms rhombic prisms, melting at 152°. It is unaffected by boiling caustic potash solution or by nitric acid. Ammonia reacts upon phlorobromin, producing bromoform and a body which has the formula $C_5H_4Br_6N_2$. Warm alcohol dissolves phlorobromin; if water be added after a time, two bodies are obtained. One is an oil which is under investigation; the other is pentabromacetone.

M. M. P. M.

Constitution of Oxythymoquinone. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 49—51).—For the melting point of this compound the author substitutes 173—174° for 187°, the temperature assigned by Carstanjen. He also calls in question Liebermann's formulæ for diamidothymol and oxythymoquinone, since they involve the explanation of the passage of the former into the latter compound by supposing that the removal of an H-atom from one OH-group is accompanied by the introduction of a second OH-group into the same molecule. The author is engaged in researches with the view of verifying experimentally the truth of his view. C. F. C.

The Constitution of Oxythymoquinone. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 77—80).—The author brings forward the following experiments in support of his views on the constitution of oxythymoquinone:—

1. Amidothymol prepared from nitrosothymol is converted into thymoquinone by the action of ferric chloride or dilute chromic acid solution. In this case a quinone group replaces an amido- and a hydroxyl-group.

$$C_{10}H_{12}\left\{\begin{matrix}OH\\NH_2\end{matrix}\right. \qquad\qquad C_{10}H_{12}\left\{\begin{matrix}O\\O\end{matrix}\right>$$

Amidothymol. Thymoquinone.

2. Nitrosothymol can be converted into dinitrothymol and oxythymoquinone, which are shown by their melting points and crystalline form to be identical with the ordinary compounds.

The composition of this group of bodies may be represented thus:—

	1.	2.	3.	4.	5.	6.
Nitrosothymol	C_6CH_3	C_3H_7	OH	NO	H	H
Nitrothymol	C_6CH_3	C_3H_7	OH	NO_2	H	H
Amidothymol	C_6CH_3	C_3H_7	OH	NH_2	H	H
Thymoquinone	C_6CH_3	C_3H_7	O	O	H	H
Dinitrothymol	C_6CH_3	C_3H_7	OH	NO_2	NO_2	H
Oxythymoquinone ...	C_6CH_3	C_3H_7	O	O	OH	H

W. C. W.

Action of Neutral Potassium Sulphite on the Quinones. By E. CARSTANJEN (*Journ. pr. Chem.* [2], xv, 478—480).—By the action of a warm concentrated solution of neutral potassium sulphite, paracymenequinone yields a new body of the formula $C_{10}H_{13}SO_5K$, crystallising in fine crystals, readily soluble in water. The author considers it to be the potassium salt of a new acid of the constitution $C_6(CH_3)(C_3H_7).SO_2.OK.H(OH)_2$. The solution of this salt is decomposed by hydrochloric and dilute sulphuric acid with the formation of sulphuric acid and hydroparacymenequinone. Caustic alkalis convert it into the corresponding acid $C_{10}H_{12}O_3$. The potassium salt of the new acid gives a fine emerald-green coloration with ferric chloride and with lead acetate a white flocculent precipitate, which is insoluble in acetic acid, but soluble in nitric acid. E. N.

On the Catechins. By A. GAUTIER (*Compt. rend.*, lxxxv, 342—345).—The author considers that the difference in composition of catechin, found by several investigators, may be accounted for by the fact that, although presenting many points of analogy, the body extracted from its various sources does possess a differing constitution according to the source from which it is obtained. He finds for the catechin of the yellow catechu of Bengal—

			Theory for $C_{21}H_{18}O_8$.
C	63·03	63·15	63·31
H	4·62	4·54	4·52
O	32·35	32·31	32·17

It melts to a viscous state from 188° to 191°. Catechin from a brown catechu from India (*Pega Cachou*), the produce of *Acacia catechu*, gave—

C..........	62·97..........	63·17
H	4·15..........	4·60

This gives the composition $C_{21}H_{18}O_8$, like the preceding, but is different in its properties, melting at 140°. It loses water of crystallisation *in vacuo*, while the variety first described does not. It is also found to contain $4H_2O$ instead of $3H_2O$. Catechin from mahogany gave on analysis the following numbers:—

	Dried at 100°.	Dried at 135°.	$C_{12}H_{18}O_8$.	$C_{42}H_{34}O_{16}$.
C	63·29	63·10	63·32	63·48
H	4·31	4·39	4·52	4·28
O	32·40	32·51	32·16	32·04

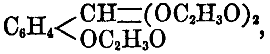
The author considers that the formula $C_{42}H_{34}O_{16}$ expresses best the composition of the sample, which he considers to be the result of duplication of the preceding ones with loss of H_2. Dried *in vacuo* it loses water. After mentioning analyses given by Schutzenberger, Rack, and others, he concludes that these analyses point to several bodies which have up to the present been considered identical, and points out that none of these numbers correspond very exactly with the formula $C_{19}H_{18}O_8$, adopted by Hlassiwetz and by the majority of chemists. J. M. T.

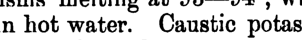
α-Toluenedisulphonic Acid. By R. GNEHM (*Deut. Chem. Ges. Ber.*, x, 1276).—When toluene-vapour is passed into sulphuric acid heated to 240°, a violent reaction takes place, resulting in the formation of toluenedisulphonic acid, together with a considerable quantity of monosulphonic acid. These products are separated by mixing the aqueous solution of their barium salts with alcohol, which throws down barium disulphonate, $C_7H_6S_2O_6Ba + H_2O$.

The disulphonic acid yields a chloride, $C_6H_3(CH_3)(SO_2Cl)_2$ melting at 52°, and an amide melting at 185°, and is thus shown to be α-toluenedisulphonic acid. J. R.

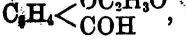
The Derivatives of Paraoxybenzaldehyde. By F. TIEMANN and H. HERZFELD (*Deut. Chem. Ges. Ber.*, x, 63—70).—*Anisic aldehyde* (methylparaoxybenzaldehyde), $C_8H_8O_2$, obtained by acting on a mixture of paraoxybenzaldehyde and caustic potash dissolved in methyl alcohol, with methyl iodide, boils at 248° and is identical with the anisic aldehyde prepared by the oxidation of anethol.

Acetylparaoxybenzaldehyde.—A mixture of 2 parts of paraoxybenzaldehyde and 1 part of caustic potash dissolved in water is evaporated to dryness; 3 parts of the residue suspended in ether are mixed with 2 parts of acetic anhydride, and the mixture is left at rest for 24 hours. On decanting the ethereal solution and evaporating, acetylparaoxybenzaldehyde remains in the form of a colourless oil, which boils at 264—265°, and does not solidify at − 21°. This body forms an insoluble compound with acid sodium sulphite, and gives a red coloration with strong sulphuric acid. It is decomposed by caustic potash into acetylparaoxybenzaldehyde and acetic acid.

Acetylparaoxybenzaldehydo-acetic acid,  $C_6H_4<\begin{matrix}CH{=}(OC_2H_3O)_2\\OC_2H_3O\end{matrix}$, is prepared by heating paraoxybenzaldehyde with acetic anhydride, or by the direct union of acetic anhydride with acetylparaoxybenzaldehyde. It crystallises in white prisms melting at 93—94°, which dissolve in ether, in hot alcohol, and in hot water. Caustic potash decomposes it into acetic acid and paraoxybenzaldehyde.

Acetylparacoumaric acid,  $C_6H_4<\begin{matrix}CH{=}CH{-}COOH\\OC_2H_3O\end{matrix}$, formed by heating a mixture of fused sodium acetate, acetic anhydride and the sodium salt of paraoxybenzaldehyde, crystallises in slender needles, soluble in alcohol, ether, glacial acetic acid, and boiling water, and almost insoluble in cold water, benzene, and chloroform. This acid melts at 195°, but begins to sublime 20 degrees below its melting point.

Fusion with caustic potash converts this body into acetic acid and paracoumaric acid; the latter substance melts at 206°, and is identical with the paracoumaric acid from aloes.

The preparation of coumarin from salicyl-aldehyde resembles that of acetyl-paracoumaric acid from paraoxybenzaldehyde. It is probable that the formation of coumarin takes place in two or even three stages. Acetylsalycyl-aldehyde,  $C_6H_4<\begin{matrix}OC_2H_3O\\COH\end{matrix}$, is the first product of the reaction. It is undecided whether this body loses water, directly forming coumarin, $C_6H_4<\genfrac{}{}{0pt}{}{O\text{————}}{CH=CH}>CO$, or whether it first forms acetylcoumaric acid, which splits up into acetic acid and coumarin.

The preparation of cinnamic acid by the action of acetic anhydride and sodium acetate on benzoic aldehyde is also described. (See Perkin, this *Journal*, 1877, i, 389.) W. C. W.

Orthotoluic Aldehyde. By B. RAYMAN (*Bull. Soc. Chim.* [2], xxvii, 498—499).—Orthotoluic aldehyde, $C_6H_4\begin{cases}CH_3\\COH\end{cases}$, is prepared by boiling orthoxylyl chloride with a solution of lead nitrate until red fumes are no longer evolved. The ethereal extract yields a yellow liquid, giving the reactions of the aldehydes, and boiling at 200°. On reduction it yields orthotoluic alcohol, and probably hydrotoluoïn.

Orthoxylene dichloride, when treated in a similar manner, yields phthalic aldehyde. L. T. O'S.

On certain Derivatives of Cuminaldehyde. By ALF. RAAB (*Deut. Chem. Ges. Ber.*, x, 52—55).—The author has prepared cuminylthiocarbimide; it is a colourless liquid, which begins to boil at 245°, and at 270° is decomposed with evolution of H_2S,HCN and CN.SH. Left in contact with ammonia for some time it forms thiosinamine; it combines with cuminylamine to form dicuminylthiocarbimide. The latter compound is also obtained by boiling the alcoholic solution of cuminylamine cuminylthiocarbamate. It crystallises in white shining needles, which melt at 128°. By the action of nascent hydrogen upon cuminaldehyde, hydrocuminoïn $C_9H_{11}.OH.CH—CH.OH.C_9H_{11}$, is formed. It occurs in small, white needles, melting at 131°, which are soluble in alcohol and ether, but insoluble in water. The author has prepared the diacetyl-derivative, $C_{20}N_{24}.(OC_2H_3O)_2$ (m.p. 143—144°), and the dichloride, $C_{20}H_{24}Cl_2$ (m.p, 184—185°), of this body.

By the action of concentrated nitric acid, hydrocuminoïn is oxidized to the compound $C_{20}H_{24}O_2$ (m.p. 138°), which the author regards as cuminoin. C. F. C.

Vapour-density of Piperonal. By W. KNECHT (*Deut. Chem. Ges. Ber.*, x, 1274).—The vapour-density of this substance is found by the author to be 5·181. The theoretical density required for the formula, $CHO—C_6H_3=OO=CH_2$, is 5·183. J. R.

Action of Sulphuric Acid upon a mixture of Benzoic and Gallic Acids. By C. SEUBERLICH (*Deut. Chem. Ges. Ber.*, x, 38—43).—As a product of the above reaction, the author obtains a body of the composition $C_{14}H_8O_5$, which, on oxidation with nitric acid, yields phthalic acid. The same compound is formed by the action of sulphuric acid on a mixture of pyrogallol and phthalic anhydride. Hence it is regarded by the author as a trihydroxyl-anthraquinone, and is termed *anthragallol*. Treated with sodium-amalgam it yields alizarin; with sulphuric acid and manganese oxide, purpurin. The constitution of anthragallol is probably the following:—

$C_6H_4.(CO)_2H(OH)_3$ (1, 2, 3). C. F. C.

Derivatives of Paraoxybenzoic Acid. By OSCAR HARTMANN (*J. pr. Chem.* [2], xvi, 35).—The author describes first a method of preparing pure potassium phenate by adding solid caustic potash to phenol heated in a shallow basin. The mixture is evaporated with constant stirring, and the heat is removed before the mass has assumed a chocolate-brown colour, else it decomposes to a great extent spontaneously. To prevent this decomposition, which is assisted by the action of air, the mass while warm should be immediately transferred to a stoppered bottle.

By the action of carbonic anhydride at 180°, potassium phenate is converted into paraoxybenzoate of potassium. The only precaution to be observed is to warm the salt gently to 180° before passing in the gas. If large quantities are required, an iron retort, provided with an apparatus for stirring is a necessity. The best fuel is peat, for the heat can therewith be kept more constant (and lower) than with any other. The paraoxybenzoic acid is precipitated with hydrochloric acid. The yield is 80 to 90 per cent. of the quantity calculated from the potassium phenate. It forms crystals belonging to the monoclinic system, the detailed measurement of which is given. The formulæ of the salts prepared by the author are as follows:—

$C_6H_4(OH)CO.ONa + 5H_2O$; $C_6H_4(OH)CO.OK + 3H_2O$;
$C_6H_4(OH)CO.ONH_4 + H_2O$; $(C_6H_4(OH)CO.O)_2Ca + 4H_2O$;
$(C_6H_4(OH)CO.O)_2Ba + 2H_2O$; $(C_6H_4(OH)CO.O)_2Cd + 4H_2O$, and $6H_2O$;
$(C_6H_4(OH)CO.O)_2Zn + 8H_2O$.

The ethylic ether was prepared by the usual method with alcohol and hydrochloric acid; it is a crystalline solid, sparingly soluble in boiling water, easily soluble in alcohol and in ether; soluble with difficulty in chloroform and benzene, and almost insoluble in carbon disulphide. It melts at 116°.

It was converted into the amide by heating 10 grams with 35 grams of ammonia of 33 per cent. to 130° for 10 hours in a sealed tube. The yield is about half the weight of the ether used. The *amide*, $C_6H_4(OH)CO.NH_2 + H_2O$, crystallises from a quickly cooled aqueous solution in long hair-like needles; and when cooled slowly, in needles with rhombic section, often 3 or 4 mm. in length. It is easily soluble in alcohol and in hot water, dissolves with difficulty in ether and in cold water, and is almost insoluble in chloroform, carbon disulphide, and benzene. It melts at 162°. Its aqueous solution has a feeble acid reaction; nevertheless, it forms with 2HCl a salt, which dissolves in water and decomposes when heated. It also forms a sodium salt, in which the hydrogen of the hydroxyl is replaced by sodium. The salt dissolves in alcohol and water. but not in ether.

The nitril was obtained by heating the amide with phosphoric anhydride. The yield is only about a tenth part of the weight of the amide used. The crude nitril is a heavy oil, mixed with phenol; the latter is evaporated off by boiling the mixture with water. The nitril then crystallises. If water containing excess of the nitril be warmed, all the impurities remain in the last drop or two of oil; the solution may be poured off, and the pure nitril crystallises out on cooling. Its formula is $C_6H_4(OH)CN$. It dissolves easily in alcohol, ether, and chloroform; it is as usual converted into the corresponding acid by boiling potash, also by hydrochloric acid. It forms salts by virtue of the hydroxyl group which it contains. The sodium salt is soluble in alcohol and water, but not in ether.

This cyanophenol strongly resembles Griess's metacyanophenol, but has little resemblance to Limpricht's salicylimide, which is also supposed to be a nitril. On these grounds, it is doubtful whether Limpricht's substance is a true nitril of salicylic acid. Paracyanophenol melts at 113°. W. R.

Derivatives of Uvitic Acid. By C. BÖTTINGER (*Liebig's Annalen*, clxxxix, 171—182).—A recapitulation and verification of results previously obtained: see this *Journal*, 1876, vol. ii, p. 414. For the α-nitro derivatives of uvitic acid the formula, $CH_3 : NO_2 : COOH : COOH = 1 : 2 : 3 : 5$, and for the β-nitro derivatives, the formula $CH_3 : COOH : NO_2 : COOH = 1 : 3 : 4 : 5$, is suggested.

M. M. P. M.

Carbousnic Acid. By O. HESSE (*Deut. Chem. Ges. Ber.*, x, 1324—1327).—Years ago Hesse discovered in *Usnea barbata* a new acid, which he called carbousnic acid, giving to it the formula $C_{19}H_{15}O_8H$ acid; and this body he fonnd split up into carbonic anhydride and usnic acid, to which last he gave the formula, $C_{18}H_{17}O_7H$—a formula confirmed by Stenhouse (*Ann. Chem. Pharm.*, cxxxvii, 241, and clv, 53). Lately, H. Salkowski (*Chem. Soc. Jour.*, 1876, i, 599) and E. Paternò (*ibid.*, 1876, ii, 202) have questioned these statements, and ascribe to usnic acid the formula $C_{18}H_{15}O_7H$, and thus invalidate the formulæ of carbousnic acid; Paternò indeed considers this last acid to be merely impure usnic acid. Hesse has therefore reprepared his carbousnic acid, a free crystalline body, giving on analysis C = 61·74 and H = 4·20. His formula, $C_{19}H_{18}O_8$, requires C = 61·29 and H = 4·30, whilst his formula for usnic acid, $C_{18}H_{18}O_7$, requires C = 62·43 and H = 5·20, and Paternò's formulæ, $C_{18}H_{16}O_7$, requires C = 62·79, H = 4·65. ($C_{17}H_{14}O_7$ would agree still better with the analytical numbers, but is invalidated by the constitution of the potassium salt.) The potassium salt crystallises from strong alcohol in yellow prisms, with 1 molecule of water, and containing K = 9·46. (Theory requires 9·15 for $C_{19}H_{15}O_8K + H_2O$); and from spirit in yellow plates with molecules of water, and containing K = 8·97). (Theory requires 8·47 for $C_{19}H_{15}O_8K + 3H_2O$). This entirely confirms the statements of Hesse, which had been questioned.

Hesse has discovered in the mother-liquors from carbousnic acid a new acid, *usnetic acid*, to which he gives the formula, $C_9H_{10}O_3$. It has, therefore, several isomerides. It consists of white anhydrous prisms, melting at 172°, readily soluble in alcohol and ether, only slightly soluble in chloroform, and insoluble in petroleum spirit. Its alcoholic solution gives a deep blue-violet colour with ferric chloride.

E. N.

The Tannic Acid of Guarana. By F. V. GREENE (*Pharm. J. Trans.* [3], viii, 328).—In extracting caffeine from guarana, several of the reactions of the accompanying tannic acid were found to be dissimilar to the other known tannic acids. Its isolation was effected by exhausting guarana with 75 per cent. alcohol, evaporating off the alcohol, and precipitating the aqueous solution with basic lead acetate. From the lead precipitate, when decomposed in the usual manner with hydrogen sulphide, was obtained an amorphous, slightly yellow, semi-transparent, partially scaly mass, which had the peculiar taste of tannic acid. It is readily soluble in alcohol, from which it separates in an amorphous condition on spontaneous evaporation of the alcohol. Acicular crystals were obtained by evaporation of its aqueous solution over sulphuric acid. As its reactions with various reagents are so dissimilar to those of any of the other tannic acids, the author concludes that the tannic acid of guarana differs from them in chemical composition; it is suggested to call it *Paullini-tannic acid.* A. J. C.

The Presence of Tannin in Gentian Root. By VILLE (*Pharm. J. Trans.* [3], viii, 182).—The author confirms the statement of Patch as to the presence of tannin in gentian root. Cold macerations of *Gentiana burseri* gave positive indications of tannin with the various reagents. Having isolated the colouring principle, gentianin, and the bitter principle, gentio-picrin, he found that the former gave tannin reactions of considerable intensity, but he obtained negative results with gentio-picrin. It is therefore proposed that gentianin shall be called *gentiano-tannic acid.* A. J. C.

Œnotannin. By A. GAUTIER (*Bull. Soc. Chim.* [2], xxvii, 496—498).—Œnotannin, or tannin of wine, is obtained from wine, after the removal of the colouring matter, in small colourless crystals, by precipitation with carbonate of copper and decomposition of the precipitate by sulphuretted hydrogen. It is soluble in water, alcohol, and ether, and in presence of alkalis it readily oxidises, its colour changing to brown. With ferric chloride it gives a bottle-green precipitate. It precipitates lead, mercury, and zinc salts, and reduces ammoniacal silver solutions.

It oxidises in the air, forming (*a*) a pink colouring matter, which appears to be identical with the red colouring matter of wine; and (*b*) a brown colouring matter, apparently identical with that of the dregs.

By the reduction of the colouring matter of wine a colourless compound is obtained. The author, therefore, thinks it is probable that the red colouring matter is a product of the oxidation of œnotannin.

L. T. O'S.

Quebracho, a New Tanning Material. By F. JEAN (*Bull. Soc. Chim.* [2], xxviii, 6—7).—Quebracho, a wood obtained from South America, is rich in tannin and in an acid analogous to tannin, and appears to act as an excellent substitute for the bark of the oak. The aqueous decoction is faintly acid, and has a reddish-yellow colour. Its reactions, which resemble those of gallic acid, are as follows:—Ferrous salts produce a bluish-black precipitate; ferric salts a dirty maroon precipitate; copper sulphate a yellowish-blue precipitate; lead acetate a pinkish-white precipitate; baryta-water no precipitate. Caustic potash produces a cloudiness; and silver nitrate in the presence of ammonia produces on warming a red coloration and a purple precipitate. L. T. O'S.

A New Derivative of Indigotin. By P. SCHÜTZENBERGER (*Compt. rend.*, lxxxv, 147—149).—Indigotin was heated for 48 hours at 180° with barium hydrate, zinc powder, and water. The residue yielded to alcohol a resinous matter, from which, when heated with zinc powder, the new body sublimed in the form of yellow acicular crystals, fusible at 245°, and soluble in alcohol and ether, but not in water. The author gives this substance the name of *induline*, and concludes from his analysis that its formula is $C_{16}H_{14}N_2$. It forms with acids well-defined crystalline compounds, and its hydrochloric acid solution affords a crystalline precipitate with platinic chloride.

R. R.

Synthesis of Indol. By ADOLF BAEYER and HEINRICH CARO (*Deut. Chem. Ges. Ber.*, x, 1262—1265).—The authors announced in a previous paper that indol is produced when ethylaniline vapour is passed through a red-hot tube. Further experiment has shown that other similar derivatives of aniline likewise yield indol, the best result being obtained with diethylorthotoluidine. When the vapour of this substance is driven rapidly through a porcelain tube filled with pumice and heated to redness, a combustible gas escapes, and a brown oily liquid containing indol collects in the receiver. From this oil the indol was separated by means of picric acid, which forms with it a crystalline compound readily decomposable by ammonia. Diethylorthotoluidine yields by this process 3—5 per cent. of pure indol. The subject is being continued. J. R.

Chlorination of Diphenyl. By J. G. KRAMERS (*Liebig's Annalen*, clxxxix, 142—145).—By direct chlorination of diphenyl in presence of antimony chloride, the author has obtained ortho- and para-chlorodiphenyl and para-dichlorodiphenyl. He has not succeeded in preparing by this means orthodichlorodiphenyl.

Orthochlorodiphenyl forms monoclinic double pyramids, $\pm P$, with the faces ∞P, $\infty \rlap{-}P \infty$, and $0P$. It melts at 34°, and boils at 267—268°. It is very soluble in benzene and in petroleum ether. This substance is very stable; it is dissolved by fuming sulphuric acid, with formation of mono- and disulpho-acids.

Parachlorodiphenyl melts at 75·5°, and boils at 282°. Paradichlorodiphenyl melts at 148° and boils at 315°. M. M. P. M.

Naphthalene-derivatives. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 1232).—*Trinitronaphthol*, $C_{10}H_4(NO_2)_3OH$, is formed on heating dinitronaphthol to 30—40° with excess of a mixture of concentrated and fuming nitric acid. It melts at 176°. The free substance and its salts crystallise with great facility, and are even more brilliant in colour than dinitronaphthol.

Dioxynaphthalene may be obtained in large quantities by fusing α-naphthalene-disulphonic acid with potash, best in an oil-bath at 280—300°, in an atmosphere of hydrogen.

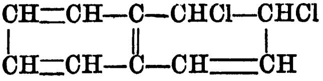
Dibenzyl-, *dibenzoyl-*, and *dimethyl-dioxynaphthalene* all crystallise well. J. R.

Hex- and Octohydronaphthalene. By J. WREDEN and B. ZNATOVICZ (*Chem. Centr.*, 1877, 6—7).—These compounds, formed by the action of hydriodic acid and amorphous phosphorus on naphthalene, are colourless, readily mobile liquids, having an odour of petroleum, and absorbing oxygen from the air. This latter circumstance probably depends on the unsymmetrical proportions in which the various carbon atoms of the benzene ring are united; thus, for instance, tetrahydroisoxylene absorbs oxygen, while hexhydroisoxylene, like decahydronaphthalene, may be kept without alteration in the air or in oxygen. By adding Berthelot's dihydronaphthalene, we obtain the following isologous series of hydronaphthalene hydrocarbons:—

	Sp. gr at 0°.	B. p.
$C_{10}H_{10}$........	—	205°
$C_{10}H_{12}$........	0·995	201° (201°)
$C_{10}H_{14}$........	0·952	197° (195°)
$C_{10}H_{16}$........	0·910	187° (187°)
$C_{10}H_{18}$........	0·857	177° (177°)
$C_{10}H_{20}$........	0·802	155°

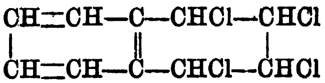
By calculating, for the four middle members of the series, the progressively increasing differences in the boiling points according to the formula $d = 4 + 2 \times n$, we obtain values (bracketted) which agree closely with those actually found. The specific gravities mentioned seem to show that for every additional H_2 the specific gravity is lowered about 0·04 to 0·05. D. B.

Chlorine Derivatives of Naphthalene. By O. WIDMAN (*Bull. Soc. Chim.* [2], xxviii, 505—512).—*Naphthalene dichloride*, $C_{10}H_8Cl_2$, is a heavy oil, to which the author assigns the following constitution:—



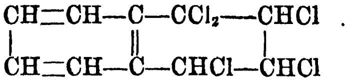
$$\begin{array}{ccccccccc} \mathrm{CH} & = & \mathrm{CH} & - & \mathrm{C} & - & \mathrm{CHCl} & - & \mathrm{CHCl} \\ | & & & & \| & & & & | \\ \mathrm{CH} & = & \mathrm{CH} & - & \mathrm{C} & - & \mathrm{CH} & = & \mathrm{CH} \end{array}$$

Naphthalene tetrachloride, $C_{10}H_8Cl_4$, melts at 182°, and according to the author has the constitution—



$$\begin{array}{ccccccccc} \mathrm{CH} & = & \mathrm{CH} & - & \mathrm{C} & - & \mathrm{CHCl} & - & \mathrm{CHCl} \\ | & & & & \| & & & & | \\ \mathrm{CH} & = & \mathrm{CH} & - & \mathrm{C} & - & \mathrm{CHCl} & - & \mathrm{CHCl} \end{array}$$

Monochloronaphthalene Tetrachlorides, $C_{10}H_7Cl.Cl_4$.—α melts at 182°, and the author gives it the following constitution:—



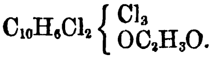
β is a yellow viscous oil, smelling like turpentine.

Dichloronaphthalene Tetrachlorides, $C_{10}H_6Cl_2.Cl_4$.—The α-compound exists in two modifications. It is crystalline, melts at 172°, and is insoluble in alcohol. B is a heavy liquid, which is soluble in alcohol.

The β-compound seems to be identical with the A-modification of the α-compound.

Trichloronaphthalene Dichlorides, $C_{10}H_5Cl_3Cl_2$.—α crystallises from alcohol in prisms which melt at 93°.

β is prepared by the action of chlorine on α-monochloronaphthalene dissolved in acetic acid. It melts at 152°. At the same time there is formed a body melting at 195°, and having the formula—



$$C_{10}H_6Cl_2\left\{\begin{array}{l}Cl_3\\OC_2H_3O.\end{array}\right.$$

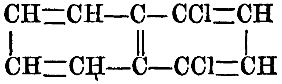
This compound is also prepared by the action of chlorine on naphthalene dissolved in acetic acid.

Substitution-derivatives.—*Monochloronaphthalenes*, $C_{10}H_7Cl$.—α an oil boiling at 293°.

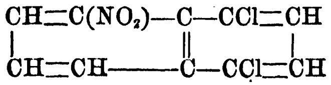
β melts between 55·5—56°.

Dichloronaphthalenes, $C_{10}H_6Cl_2$.—α melts between 35—36°, and yields a trinitro-derivative, $C_{10}H_3Cl_2(NO_2)_3$, which melts at 178°.

β melts at 67—68°, and, according to Atterberg, has the constitution—



It yields a mononitro-derivative which has the constitution—



and melts at 92°.

By reduction the nitro-compound yields an amide, the hydrochloride of which forms with stannous chloride a double salt—

$$C_{10}H_5Cl_2(NH_2).HCl + SnCl_2,$$

which yields the hydrochloride when decomposed by sulphuretted hydrogen. The free base, $C_{10}H_5Cl_2(NH_2)$, melts at 104°, and like other amines forms a series of well-defined salts.

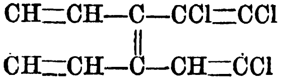
The β-compound also forms a dinitro-derivative, $C_{10}H_4Cl_2(NO_2)_2$, which melts at 158°.

γ melts at 107°, and yields a mononitro-derivative melting at 142°, and a dinitro-derivative which melts at 246°.

δ melts at 114°.

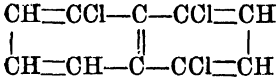
ε melts at 135°.
ζ melts at 83°.
η melts at 48°.

Trichloronaphthalenes, $C_{10}H_5Cl_3$.—α melts at 131·5°, and has the constitution—



$$\begin{array}{l}\mathrm{CH{=}CH{-}C{-}CCl{=}CCl}\\ \qquad\qquad\quad\| \\ \mathrm{CH{=}CH{-}C{-}CH{=}CCl}\end{array}$$

β melts at 90°.
γ melts at 103°.
δ melts at 131°. Its constitution is—



$$\begin{array}{l}\mathrm{CH{=}CCl{-}C{-}CCl{=}CH}\\ |\qquad\qquad\quad\|\qquad\qquad\quad| \\ \mathrm{CH{=}CH{-}C{-}CCl{=}CH}\end{array}$$

Tetrachloronaphthalenes, $C_{10}H_4Cl_4$.—α crystallises in needles which melt at 130°. By oxidation it yields dichlorophthalic acid.

β melts at 194°.
γ melts at 176°.
δ melts at 141°.

Heptachlorodinaphthalene of Faust and Saame is probably not a definite compound, as by repeated crystallisations the author has obtained two bodies, one melting at 164°, the other at 70°.

Pentachloronaphthalene, $C_{10}H_3Cl_5$.—Melts at 168·5°.

Perchloronaphthalene, $C_{10}Cl_8$.—Melts at 135° (Berthelot and Jungfleisch) and 203° (Ruoff). L. T. O'S.

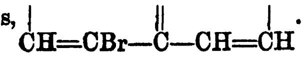
The Derivatives of γ-Dichloronaphthalene. By ATTERBERG and WIDMAN (*Bull. Soc. Chim.* [2], xxvii, 513, 514). *γ-Dichloronaphthalene tetrachloride*, $C_{10}H_6Cl_2Cl_4$, crystallises in prisms which melt at 85°. By distillation or by the action of alcoholic potash, it yields α-dichloronaphthalene dichloride. By the action of phosphorus pentachloride on the mono-nitroderivative of δ-tetrachloronaphthalene, *β-pentachloronaphthalene* is obtained, which crystallises in white plates, melting at 177°. On oxidation this body yields trichlorophthalic acid.

The dinitro-derivative of γ-dichloronaphthalene, when treated with PCl_5, yields ε-tetrachloronaphthalene, which melts at 180°.

L. T.

Some Bromine Derivatives of Naphthalene. By S. JOLIN (*Bull. Soc. Chim.* [2], xxviii, 514—518).—*Dibromonaphthalenes*, $C_{10}H_6Br_2$. By the action of bromine on naphthalene or on α-monobromonaphthalene, a mixture of the α and β compounds is obtained, the former melting at 60·5—61°, and the latter at 81°.

γ is obtained by the action of phosphorus pentabromide on α-nitronaphthalene. It melts at 129°, and according to the author its constitution is,



$$\begin{array}{l}\mathrm{CH{=}CH{-}C{-}CBr{=}CH}\\ |\qquad\qquad\quad\|\qquad\qquad\quad| \\ \mathrm{CH{=}CBr{-}C{-}CH{=}CH}\end{array}.$$

β-dibromonaphthalene yields a mononitro-derivative, which, when treated with PBr_5, yields β-dibromonaphthalene, which melts at 85°.

Transformation of Naphthionic acid into $C_{10}H_6Br_2$.—By treating diazonaphthionic acid (Cleve) with HBr, or distilling potassium bromonaphthyl sulphite with PBr_5, β-dibromonaphthalene is obtained. If PCl_5 is used instead of PBr_5, β-dichloronaphthalene is the result.

α-Bromonaphthylsulphurous acid, $C_{10}H_6BrSO_2OH$, prepared by the action of sulphuric acid on α-bromonaphthalene, forms a chloride, $C_{10}H_6BrSO_2Cl$, melting between 86—87°, an amide, $C_{10}H_4BrSO_2(NH_2)$, melting at 190°, and a bromide, $C_{10}H_6BrSO_2Br$, which, like the potassium salt of the acid, yields β-dibromonaphthalene, when treated with PBr_5.

Once the author obtained ϵ-dibromonaphthalene, by the action of PBr_5 on the sulpho acid of α-monobromonaphthalene.

α-Dinaphthylsulphurous acid, when treated with bromine, yields a dibromo-acid, which forms a chloride melting at 90°, and an amide melting between 237—238°. The potassium salt of this acid, when treated with PBr_5, yields γ-tribromonaphthalene, which melts at 86·5°.

α-Naphthyldisulphurous acid, $C_{10}H_6(SO_3H)_2$, when treated with PBr_5, yields δ-dibromonaphthalene.

By comparing the melting points of the corresponding dibromo- and dichloronaphthalenes, we find the following differences:—

	$C_{10}H_6Br_2$.	$C_{10}H_6Cl_2$.	Difference.
α....	60·5—61°	35·5—36°	25·5—25°
β....	80·5—81°	68°	12·5—13°
γ....	107°	129°	22°
δ....	140·5°	114°	26·5°
ϵ....	159·5° (?)	135° (?)	29·5°

L. T. O'S.

Derivatives of Phenanthrene. By R. STRUVE (*Deut. Chem. Ges. Ber.*, x, 75—76).—*Dinitrophenanthraquinone* is a yellow powder, insoluble in most solvents, but slightly soluble in acetic acid. It dissolves easily in melted naphthalene, and is left in the form of leafy crystals, when the fused mass is treated with ether. Strong oxidising agents convert it into *dinitrodiphenic* acid, a white powder, slightly soluble in ether and in cold water; more soluble in hot water and in alcohol. The barium salt, $C_{14}H_6N_2O_8Ba + 6H_2O$, forms long prismatic crystals; the silver salt is a white powder.

Diamidodiphenic acid, formed by the action of reducing agents on the preceding acid, is a white amorphous powder, melting at 250—251°. It is but slightly soluble in the ordinary solvents; its ammonia salt is very soluble. By heating the hydrochloride of this acid with soda-lime, a diamidodiphenyl is obtained, which melts at 155—157°, gives with potassium ferrocyanide a blue precipitate insoluble in acids and in hot water, and forms with chlorine-water, first a blue, then a green, and finally a reddish-brown coloration.

The author regards this body as an isomeride of benzidine, and considers that the *diamidodiphenic* acid, prepared by Griess from metanitrobenzoic acid (this *Journal*, 1875, 460), is not identical with that obtained from phenanthrene.

W. C. W.

Oxidation of Camphor. By J. DE MONTGOLFIER (*Compt. rend.*, lxxxv, 961—964).—Camphor when slowly oxidised yields, as first product, monobasic camphic acid, $C_{20}H_{16}O_2$, which is readily oxidised to camphoric acid, yielding at the same time a small quantity of an intermediate product. Under certain circumstances camphic acid yields on oxidation an acid, called *phoronic acid*, $C_{18}H_{16}O_2$. L. T. O'S.

Note on Yellow Amber. By M. REBOUX (*Ann. Chem. Phys.* [5], xi, 138—144).—The principal differences which exist between natural and artificial amber, and copal, are as follows:—

In the same specimen copal possesses a uniform yellow colour, but in natural amber the tint varies.

Natural amber when rubbed evolves an aromatic odour; copal and artificial amber do not.

Natural amber, by long exposure to the air, sometimes loses an essential oil, and its characteristic appearance.

When natural amber is greased and warmed, it can be bent; but copal and artificial amber cannot.

Natural amber is harder than artificial amber and copal.

Copal melts at a low temperature without change in colour, and at 100° it gives off considerable quantities of moisture, whereas natural amber does not melt at 400°, but blackens, and gives off suffocating gases; if, however, it is mixed with linseed oil, it melts at 150°.

The density of natural amber is 1·09—1·11; that of copal, 1·04; and that of artificial amber, about 1·05; but it varies.

On distillation copal does not yield succinic acid, like natural amber. The following are the results of an analysis of yellow amber, by Schrötter:—

Carbon, 78·82. Hydrogen, 10·23. Oxygen, 10·90.

L. T. O'S.

Some further Experiments upon the Aloïns. By W. A. TILDEN (*Pharm. J. Trans.* [3], viii, 231). Nataloïn digested with potassium bichromate and sulphuric acid, yields CO_2, acetic acid, and probably quinone. Barbaloïn and socaloïn, both of which have the same composition, give with potassic bichromate, CO_2, acetic acid, and a yellow compound which the author calls *aloxanthin*. After purification by repeated crystallisation from alcohol, acetic ether, and glacial acetic acid, this substance gave on analysis numbers agreeing with the formula, $C_{15}H_{10}O_6$. Heated with zinc dust, it is reduced to methylanthracene, thus showing it to be a methyltetroxyanthraquinone, $C_{14}H_3(CH_3)(OH)_4O_2$. This formula belongs to a third term in the same series as chrysophanic acid and emodin. With alkalis, aloxanthin produces a cherry-red solution, and with strong nitric acid in the cold, a yellow nitro-compound, having all the characters of Schunck's aloetic acid, which is formed, together with chrysammic acid, by the action of nitric acid on aloes; the continued action of boiling nitric acid yields chrysammic acid. A. J. C.

Cyclamin, Primulin, and Primula-Camphor. By L. MUTSCHLER (*Liebig's Annalen*, clxxxv, 214—223).—The author has examined cyclamin extracted from cyclamen bulbs by 70 per cent. alcohol. After treatment with animal charcoal, it forms a dazzling white powder, or white granules made up of microscopic needles. It is very hygroscopic, easily soluble in weak spirit, and more or less soluble in methyl and amyl alcohols, ethyl acetate, and glycerin; insoluble in ether, chloroform, carbon bisulphide, benzene, and petroleum spirit. Cyclamin is inodorous, but has an extremely acrid and bitter taste; and its dust excites violent sneezing. It turns brown at 100° and melts at 236°. The aqueous solution is opalescent, froths like soap-water, and produces a white precipitate in alkaline solution of cupric oxide, but does not reduce copper, even on long boiling. Strong sulphuric acid dissolves cyclamin with red colour; on diluting the solution with water, the colour disappears, and a white precipitate of cyclamiretin is thrown down, glucose remaining in solution. This decomposition of cyclamin into cyclamiretin and sugar is effected also by heating its aqueous solution to 95° for some time; by heating the dry substance to 100°; by prolonged exposure of the solution to direct sunshine; by the action of emulsin or beer-yeast; but most easily and completely by the action of dilute hydrochloric acid.

Cyclamin closely resembles saponin in physical and chemical characters, and is probably identical with it.

Cyclamiretin is a white, amorphous, inodorous, and tasteless powder, dissolving in alcohol and ether, but not in water, and melting at 198°. It is coloured violet by sulphuric acid. Its composition agrees with the formula, $C_{15}H_{22}O_2$. By fusion with potash it yields formic and butyric acids and other products. Nitric acid acting upon it produces resinous bodies, and ultimately oxalic acid.

Primulin.—The substance extracted from primula-roots by alcohol, and thus named by Hünefeld, is found by the author to be nothing but cyclamin.

Primula-Camphor.—This substance, obtained by the distillation of primula-roots, separates from the distillate, after standing, either in shining hexagonal laminæ, or in the form of a semi-solid, oily mass. It smells like fennel or anise; tastes at first burning, afterwards sweet, melts at 49°, and distils above 200° without decomposition. The camphor dissolves sparingly in water, but easily in alcohol and ether; the aqueous solution is coloured violet by ferric chloride. Its composition agrees with the formula, $C_{22}H_{24}O_{10}$. It yields salicylic acid by boiling with potash-ley. J. R.

The Chemical Constituents of "Convolvulus Scammonia."

By C. T. KINGZETT and T. FARRIES (*Pharm. J. Trans.* [3], viii, 249).—The roots were extracted with hot water, then with 85 per cent. of alcohol, and finally with ether. The aqueous extract contained no alkaloïd. From alcohol was obtained a yellow stringy mass soluble in ether, giving when purified the purple reaction with sulphuric acid and with sulphuric acid and sugar. Its barium compound gave on analysis numbers wherein Ba : H as 1 : 19·5 atoms. There can be little doubt that it represents an intermediate state occurring in the spontaneous change of glucosate into glucinate of barium. Of its relation to sugar, the authors believe there is no question. The same substance may be obtained by submitting to a similar treatment the retort-residue from the dry distillation of scammony resin. Scammony resin is said, therefore, to be a glucoside, and to yield glucose by proper treatment. A. J. C.

Phyllic Acid, a New Substance contained in the Leaves of certain Plants. By C. BOUGAREL (*Bull. Soc. Chim.*, xxviii, 148).—In trying to extract amygdalin from the leaves of certain plants of the rosaceous order, especially the cherry-laurel, a new substance was discovered which subsequently was found in many other plants. It is found in the alcoholic extract of the leaves, and, after purification, forms colourless crystalline granules, soluble in alcohol, ether, chloroform, and carbon bisulphide, insoluble in water. Sp. gr. about 1·014. Its specific rotatory power in alcoholic solution is $\alpha = +28°$. This substance (phyllic acid) melts at 170° and solidifies on cooling in flat prisms terminated by pyramids of about 120°. When heated above 180° it decomposes, giving off white fumes of balsamic odour, which condense in oily drops.

Dilute acids have no effect on this body.

In contact with cold potash, it does not apparently dissolve, but combines slowly, with formation of a body crystallising in prismatic needles with square base.

These needles, which are the potassium salt of phyllic acid, are slightly soluble in cold water, soluble in hot slightly alkaline solutions, insoluble in strong alkalis; soluble in alcohol, ether, and chloroform. When treated with hydrochloric acid, they give a body having the properties of the original acid, except that its rotatory power is different, $\alpha = +53°$; the rotatory power of the potassium salt in alcoholic solution is $\alpha = +56°$.

Analysis gave the following numbers: $C = 69·08$, $H = 10·36$. An analysis of the potassium salt gave the equivalent as 624, leading to the formula $C_{36}H_{64}O_8$.

The sodium salt crystallises easily.

The ammonium salt crystallises in tufts of long slender needles.
C. W. W.

Acid of Willow Bark. By D. B. BOTT (*Pharm. J. Trans.* [3], viii, 221).—The analysis of the normal calcium and zinc salts of the acid extracted by infusion of willow bark, gave numbers nearly corresponding with the normal lactates. It is considered not improbable that lactic acid exists in all the members of the salicaceous order.
A. J. C.

Polysulphydrates of Strychnine and Brucine. By ERNEST SCHMIDT (*Deut. Chem. Ges. Ber.*, x, 1288).—Hofmann has shown that the product of the action of yellow ammonium sulphide on a cold saturated alcoholic solution of strychnine is indicated by the formula $(C_{21}H_{22}N_2O_2)_2H_2S_6$, and not by $C_{21}H_{32}N_2O_2,H_2S_3$. In order to see if the compounds of brucine with hydrogen and sulphur are analogously constituted, the author has examined them afresh; the red compound now turns out to be $(C_{23}H_{26}N_2O_4)_3(H_2S_6)_2$, and the yellow one $(C_{23}H_{26}N_2O_4)_3.H_2S_6,6H_2O$, instead of $(C_{23}H_{26}N_2O_4)(H_2S_2)_2,H_2O$ and $(C_{23}H_{28}N_2O_5).H_2S_2$ respectively, as previously stated, their new formulæ being deduced from the weights of sulphur and arsenic sulphide formed by acting on the polysulphides with arsenious acid dissolved in hydrochloric acid. Apparently the body formed by acting on brucine with sulphuretted hydrogen is identical with that produced by means of sulphide of ammonium. C. R. A. W.

Action of Sulphuric Acid and Oxidising Agents on Morphine and its Salts. By D. LINDO (*Chem. News*, xxxvi, 228).—All oxidising agents when added to morphine which has been treated with strong sulphuric acid and then diluted, develope a deep-red coloration. E. W. P.

Note.—A correspondent states that the above reaction is not characteristic of morphine, but is produced also by codeine and narcotine.

Veratrine. By ERNST SCHMIDT and RUD. KÖPPEN (*Liebig's Annalen*, clxxxv, 224—247).—The authors have examined veratrine obtained by exhausting sabadilla seeds with boiling dilute sulphuric acid, and purified by crystallisation from spirit. The crystals, which are transparent at first, soon turn turbid and opaque. They melt at 205°. The formula of the substance deduced from numerous analyses is $C_{32}H_{50}NO_9$. The following compounds were also prepared and analysed:—

Sulphate, $(C_{32}H_{50}NO_9)_2H_2SO_4$.
Hydrochloride, $C_{32}H_{50}NO_9HCl$.
Auro-chloride, $C_{32}H_{50}NO_9HCl + AuCl_3$.
Platino-chloride, $(C_{32}H_{50}NO_9HCl)_2 + PtCl_4$.
Mercuro-chloride, $C_{32}H_{50}NO_9HCl + HgCl_2$.

Isomeric Modifications of Veratrine.—Weigelin observed that solutions of veratrine in acids are only imperfectly precipitated by ammonia in the cold, and that the precipitated substance dissolves in water on prolonged washing, but is again precipitated on boiling the solution. The correctness of these observations is confirmed by the authors. On evaporating the aqueous solution in a vacuum, the soluble veratrine is left as a yellowish translucent amorphous mass, readily soluble in cold water. Ammonia throws down from the aqueous solution, at a certain stage of concentration, an amorphous precipitate of veratrine; but in presence of a small quantity of ammonium chloride the veratrine is deposited in delicate needles, iridescent in sunshine. The crystalline and soluble varieties of veratrine may thus be converted one into the other without difficulty.

There exists also a third modification of veratrine, which is amorphous and insoluble in water. It is deposited in the form of a resinous mass when a solution of veratrine in weak spirit is evaporated. When dry it is a yellowish-white substance, easily reducible to a white powder, which excites violent sneezing. It dissolves readily in alcohol and ether.

Veratrine as ordinarily prepared appears to be a mixture of the crystalline and amorphous varieties. Its solution in weak spirit, when slowly evaporated, first deposits the crystalline and afterwards the amorphous substance. In this process a portion of the latter is always converted into soluble veratrine, which may be dissolved out of the residue by water.

Eight samples of commercial veratrine from various sources, analysed by the authors, were found to be nearly pure. J. R.

Note on Pilocarpine (from Jaborandi). By C. T. KINGZETT (*Pharm. J. Trans.* [3], viii, 255).—The examination of the nitrate and the platinochloride of pilocarpine, both of which were obtained from Dr. Attfield, gave on analysis results confirming those previously obtained by the author, viz., that jaborandi yields but one alkaloïd, which appears to yield trimethylamine. A. J. C.

Action of Cyanogen on Albumin. By OSCAR LOEW (*J. pr. Chem.* [2], xvi, 60—77).—From Schutzenberger's researches, albumin has been proved to yield the following eighteen bodies, under the action of barium hydrate:—Leucine, amidopropionic, amidobutyric, and amidovaleric acids; butyric leucine, valeric leucine, caproic leucine, tyrosine, tyroleucine; glutimic, glutamic, aspartic, acetic, oxalic, carbonic, and sulphurous acids, and ammonia. As such amido-acids have a great tendency to unite with cyanogen when treated with the gas, the following experiments were made with the view of ascertaining with how much cyanogen albumin would unite, and determining the formulæ of the resulting products. The formula on which the calculation of the results was based was that of Lieberkühn, namely, $C_{72}H_{112}N_{18}SO_{22}$.

In the first experiment the cyanogen from 20 grams of mercuric cyanide was passed through 50 grams of albumin dissolved in 200 cubic centimeters of water. The sediment which settled after two days, and the precipitate caused by acetic acid in the filtrate from this sediment, have the same composition. It is amorphous, insoluble in water, alcohol, and dilute acids, but easily soluble in alkalis. From analyses, it appears to represent albumin plus one molecule of cyanogen and three of water. Its formula is therefore $C_{74}H_{118}N_{20}SO_{25}$. On treatment with caustic potash, the fourth part of the cyanogen absorbed was converted into ammonia and oxalic acid, and acetic acid then produced a dirty green precipitate.

The second experiment was conducted by passing the cyanogen from 35 grams of mercury cyanide through 50 grams of albumin dissolved in 550 c.c. of water. As before, the sediment and the precipitate with acetic acid had the same composition, but differed from the former. Its formula is $C_{76}H_{128}N_{22}SO_{30}$, and it may be viewed as albumin to which 2 molecules of cyanogen and 8 molecules of water have been added.

An attempt was made to determine whether the cyanogen was held in combination with leucine and tyrosine, by heating some of the cyanogen-compound with hydrochloric acid to 100° for thirty hours. No leucine or tyrosine cyanide was obtained, but merely the pure amido-acids.

The third experiment consisted in treating 30 grams of albumin, dissolved in 300 grams of water, four times, each time with the cyanogen resulting from the decomposition of 25 grams of mercuric cyanide. The sediment which was formed at first redissolved; and on addition of acetic acid a dark-coloured substance was thrown down, the filtrate from which, when concentrated, deposited a yellow indistinctly crystalline substance. The dark-coloured substance had the formula $C_{80}H_{144}N_{26}SO_{38}$, from which it is viewed as albumin plus four molecules of cyanogen and sixteen of water. This substance is easily decomposed, when allowed to stand in alkaline solution, into oxalic acid, ammonia, sulphuretted hydrogen, hydrocyanic acid, and carbon dioxide. The solution, over-saturated with acetic acid and filtered while boiling, deposits a yellow amorphous powder, sparingly soluble in water and in dilute acids, but readily in alkalis and sodium acetate. Its solution in ammonia gives a brownish-red precipitate with silver nitrate. This substance is soluble in hot nitric acid, and separates out partially on cooling, but still amorphous. It contains 22·42 per cent. of nitrogen. It is not produced if less cyanogen be passed through the albumin.

When 200 grams of albumin dissolved in 3,500 c.c. of water were treated in five consecutive days with the cyanogen from 100 grams of mercuric cyanide, the filtrate from the precipitate caused by acetic acid deposited on evaporation a substance soluble with great difficulty in water and alcohol, but more soluble in solutions of some salts and in acids. It has a yellow colour, and separates in crusts. It yields a white sublimate, with evolution of hydrocyanic acid; it dissolves in strong sulphuric acid, and on addition of water a yellow powder is precipitated. It gives yellow precipitates with silver nitrate and lead acetate. On boiling it with soda, ammonia and oxalic acid are produced: hence the author names the new substance *oxamoïdin*. Its formula is $C_{14}H_{23}N_{11}O_{10}$. When boiled with potash it yields quantities of ammonia and oxalic acid, which show that the body $C_9H_{16}N_9O_9$ is separated from it, leaving the group $C_5H_5N_2O$ as a residue.

The sediment in this operation, when treated with hydrochloric acid, gave a considerable amount of leucine, but very little tyrosine. The precipitate with acetic acid decomposes with excess of water. When it is boiled with caustic soda, tyrosine and leucine are formed, besides a substance precipitable by tannic acid. With weak boiling soda the usual decomposition-products are also formed; and if the solution be acidified and filtered while hot, a canary-yellow powder separates out on cooling, which the author names *cyalbidin*. When boiled with water, it cakes together, melts, and dissolves to a small amount with a yellow colour. It is easily soluble in alkaline liquids and in sodium acetate; from the latter solution it is thrown down by acetic acid. Its alkaline solution is strongly fluorescent. Its solution in strong hydrochloric acid gives a precipitate on addition of water, but not of alcohol. It dissolves slowly in strong sulphuric acid; its solution in hot strong nitric acid deposits a yellow powder on cooling. Its formula is $C_{76}H_{112}N_{22}SO_{26}$, *i.e.*, albumin plus 4CN and O_4.

When the sediment in the liquid from which cyalbidin was obtained is warmed with dilute caustic soda, it gives off a part of its sulphur as sulphuretted hydrogen, and the remaining solution, on treatment with acetic acid, deposits a canary-yellow body, not to be distinguished from cyalbidin. The liquid from which the cyalbidin had deposited gave no substances of definite composition.

From further researches, the author ascertained that urea is formed by the action of excess of cyanogen on albumin, and also that oxamoïdin is a compound of oxamide with a nitrogenous substance, soluble in alkalis, and precipitable in reddish-brown flocks by acetic acid. It is sparingly soluble in cold, and more easily in hot water, and gives a yellow precipitate with silver nitrate, insoluble in ammonia.

W. R.

Physiological Chemistry.

Distribution of the Carbonic Anhydride contained in Blood between the Corpuscles and Serum. By L. FREDERICQ (*Compt. rend.*, lxxxiv, 661—663).—It is stated in most physiological works that the whole or nearly the whole of the carbonic anhydride contained in blood is to be found in the serum. In order to test the accuracy of the above assertion, the blood of the horse was carefully defibrinated and analysed.

The results show that the red corpuscles of the blood are capable of absorbing and retaining a notable proportion of carbonic anhydride, but always less than that contained in an equal volume of serum.

Thus the total volume of carbonic anhydride obtained in one experiment from 100 c.c. of the blood was 46·8 c.c., and from 100 c.c. of serum 54·65 c.c. Admitting that in the blood of the horse, the proportion by volume of corpuscles to serum is as 3 : 7, the volume of carbonic anhydride retained by the corpuscles was one-half less than that retained by the serum.

When a current of carbonic anhydride was passed through the blood to saturation, the excess of gas was found to be equally divided between the corpuscles and the serum. In analysing serum, it is necessary that an acid, preferably phosphoric acid, be added to the liquid previous to heating in a vacuum, otherwise a very large proportion of the carbonic anhydride is permanently retained. J. W.

The Physiology of Sugar in Relation to the Blood. By F. W. PAVY (*Proc. Roy. Soc.*, xxvi, 314 and 346).—The author considers that Bernard's process for the estimation of sugar in the blood by means of Fehling's solution, is not trustworthy; first, because the volume varies with the amount of solid matter in the blood, and with the amount of evaporation; secondly, in consequence of the action of organic matter (especially in presence of potash) in preventing the precipitation of cuprous oxide.

The present process is based upon the precipitation of the suboxide, and the subsequent collection of the copper on platinum foil by means of galvanic action. The following is an outline of the method employed:—

The blood is mixed with sodium sulphate, boiled to remove albuminous and colouring matters, then filtered, and boiled with excess of copper solution; and the reduced oxide is collected and dissolved by means of hydrogen dioxide and nitric acid. A weighed cylinder of platinum foil, forming the negative pole of a battery (the positive pole being a spiral of platinum wire placed within the cylinder), is immersed in the solution, and reweighed after the complete deposition of the copper. Minute details of the process are given, for which the original paper must be consulted.

The blood to be analysed must be collected either during life, or immediately after death, and must be analysed as soon as possible after collection, as the amount of sugar rapidly decreases.

The author concludes, from the results of numerous experiments, that the amount of sugar naturally present in the blood of the sheep or bullock is about 0·05 per cent., and in that of the dog about 0·075 per cent. Bernard states that the normal amount of sugar varies from 0·1 to 0·3 per cent.

From the following experiments it seems that there is no decided difference between the amounts of sugar present in arterial and venous blood respectively:—

Sugar per 1,000 *parts.*

(1)	Crural artery.			Jugular vein.	
a.	0·799	0·795 (mean)	*a.*	0·793	0·792 (mean)
b.	0·791		*b.*	0·791	
(2)	Carotid artery.			Jugular vein.	
a.	0·806	0·811 (mean)	*a.*	0·808	0·798 (mean)
b.	0·817		*b.*	0·788	
a.	0·854	0·863 ”	*a.*	0·863	0·879
b.	0·873		*b.*	0·896	

The sugar in blood gradually diminishes in amount on standing, so that after twenty-four hours more than half of it has disappeared.

C. W. W.

The Free Acids of the Gastric Juice. By C. Richet (*Compt. rend*[illegible]xxiv, 1514—1517).—If an aqueous solution of organic and inorganic acids is shaken up with ether, Berthelot has shown (*Chem. Soc. Journ.*, 1872, 783), that the former are dissolved in the ether, whilst the latter remain, comparatively speaking, undissolved. By titrating the acidity of the two solutions, the relative amount of organic and inorganic acids present in the original mixture may be estimated.

Following this method, the author finds that pure gastric juice contains almost entirely inorganic acids, or more correctly acids insoluble in ether.

Left to itself, the gastric juice gradually ferments, and the amount of organic acid slowly increases until it doubles that of the inorganic acid.

The gastric juice having been separated from the glands of the stomach and mixed with aliment, its acidity greatly increases during artificial digestion, but the inorganic acids always predominate.

The ferment producing this acidity is partially soluble.

F. J. L.

Transformation of Glycogen into Grape-sugar by Saliva and Pancreatic Ferment. By J. Seegen (*Chem. Centr.*, 1877, 8).—It is mentioned in chemical and physiological books that saliva and pancreatic ferment transform glycogen quickly and completely into grape-sugar. The author's experiments in this direction gave opposite results, only a portion of the glycogen being converted into grape-sugar. With saliva the portion thus transformed varied from 34—41 per cent. When pancreas extract was used as ferment it amounted to 45—48 per cent. This shows either that glycogen is converted not into grape-sugar, but into a substance which reduces cupric oxide in a different proportion, or that in the conversion of glycogen another product is formed besides sugar. Which of these suggestions is correct must be ascertained by further investigations. D. B.

Digestion of Linseed-mucilage with Artificial Gastric Juice. By H. Fudakowski (*Chem. Centr.*, 1877, 6).—The author finds that by digesting linseed-mucilage with artificial gastric juice a sugar is obtained which does not yield mucic acid. By digesting arabic acid from dextro-rotatory gum with artificial gastric juice, a kind of sugar is obtained which agrees with that mentioned by Lüxinger. These experiments establish the influence of pepsin in the formation of sugar in the organism. Contrary to Lüxinger's statement, the author could not observe any direct influence of the pancreatic ferment on gum.

D. B.

Action of Sulphur on the Excretion of Sulphuric Acid in the Urine. By M. Regensburger (*Zeitsch. f. Biologie*, xii, 479—496).—In the Physiological Laboratory of Munich, T. Etzinger made a series of experiments upon dogs, which proved that sulphur, when administered in the finely divided state known as "flowers of sulphur," became slightly absorbed in its course through the body, and eliminated in the urine partly as sulphates, partly as organic sulphur-compounds.

These experiments, which are here quoted by permission of Prof. Voit, the author has repeated, and obtains like results. But the important point was to discover how and in what part of the alimentary canal the sulphur became changed and absorbed into the system.

Sulphur was mixed with each of the following substances:—Pure bile, white of egg, serum of blood; milk, both fresh and sour; pure casein, and a mixture of hæmatin solution with a glycerin extract of the pancreas. The mixtures, having been kept at a moderate temperature for some days, were subsequently tested with sodium nitroprusside, when they each gave the coloration characteristic of an alkaline sulphide. The substances themselves treated similarly, but without addition of sulphur, gave no coloration.

These experiments, out of many, mostly yielding negative results, lead to the belief that the absorption of sulphur takes place in the intestines. F. J. L.

Presence of Metallic Compounds in Alimentary Substances. By B. H. PAUL and C. T. KINGZETT (*Pharm. J. Trans.* [3], viii, 232). —*Preserved Peas and Copper.*—The amount of cupric sulphate which is added to preserved peas varies between 1 and 2 grains per tin, containing about 9½ ounces of peas per 150 c.c. of liquor. The authors find (1) that natural green peas contain no copper; (2) in the preserved peas the copper is not in the liquid, but in actual combination with the peas, and is not removed during the process of cooking. (3) Since it was found that by the artificial digestion of coppery peas with pig's pepsin, the whole of the copper passed into solution, it may be presumed that in stomachic digestion preserved peas give up their copper to the solution. (4) To ascertain whether any part or all of the copper thus introduced into the stomach is absorbed, or is eliminated, and if so, in what manner, each of the authors took a dose of 0·3 grain of cupric sulphate, but no copper was found in the urine eliminated during the subsequent 48 hours. Daily for six consecutive days, the same quantity was taken by each, but only the merest trace of copper was eliminated in the total urine. In the fæces excreted on the fourth day by one of the authors, abundant evidence of copper was found, forming a very considerable proportion of a dose.

As the quantity of peas daily consumed would contain only a fraction of a grain of cupric sulphate, of which only a fraction is absorbed into the blood system, it is impossible to defend the opinion of the prejudicial influence of such amount of copper on health. Finally the authors believe that preserved peas are absolutely innocuous to health.

Other alimentary substances containing metallic compounds.—At various times, salts of lead, of arsenic, chromium, &c., have been met with as being employed to colour various alimentary substances, and latterly the authors have examined colouring matters of French origin, containing in the dry substance from 8 to 60 and even 75 per cent. of stannic oxide. It is considered questionable whether the use of compounds containing so much tin should be admissible.

A. J. C.

Tetrachloride of Carbon, and its Use as an Anæsthetic. By C. MOREL (*Compt. rend.*, lxxxiv, 1460—1462).—The paper describes a modification in the process for preparing carbon tetrachloride. Because this compound has a greater chemical stability than chloroform, the author thinks it would be found a better anæsthetic. The physiological effects are the same, except that with the chloride of carbon, the excitement in the first stage is more marked.

R. R.

Note by the Abstractor.—The use of tetrachloride of carbon as an anæsthetic was tried many years ago.

Action of Arsenic on the Chemical Change (Metabolism) of Albumins. By H. v. BOECK (*Zeit. f. Biologie*, xii, 512).—The author objects to the experiments of Gäthgens (*Centrb. f. Med. Wiss.* 1875, 529), and denies the supposition that arsenic exerts any influence on the metabolism of albumins. F. J. L.

Chemistry of Vegetable Physiology and Agriculture.

Absorption of Bases by the Soil. By H. P. Armsby (*Amer. J. Sci.*, xiv, 25).—The author considers that the absorption of bases by the soil is due chiefly to chemical action between substances contained in the soil and the solution filtered through it. An artificial hydrous silicate containing soda and alumina was prepared and digested with varying proportions of a standard calcium chloride solution; after standing for three days, the lime was estimated in the liquid, and the absorption calculated.

The variations of absorption took place as with soil. The utmost amount of soda replaced was about two-thirds, while in those experiments in which that point was not reached, the absorption increased with the concentration in the same way as in the soil-absorption. An increase of concentration was unable to replace the remaining third of the soda, which is probably more difficult to replace.

The author therefore arrives at the following conclusions:—

The absorption of combined bases by the soil consists in an exchange of bases between the salt and the hydrous silicates of the soil. This exchange, which is primarily chemical, is only partial, and varies in extent: 1st, with the concentration of the solution; 2nd, with the ratio between the volume of the solution and the quantity of soil used.

The cause of these variations is probably the action of mass, or the tendency of resulting compounds to reform the original bodies, the absorption actually found in any case marking the point where the two forces are in equilibrium. C. W. W.

Researches on Phosphoric Acid in Arable Land. By B. Corenwinder and G. Contamine (*Compt. rend.*, lxxxv, 501).—The authors have experimented on the effect of applying superphosphate to land, and on the comparative solubility of natural and artificial phosphates. They come to the following conclusions:—

The phosphates contained in the soil are not equally soluble in water containing carbonic acid. Their capacity in this respect depends on their state of combination and the source from which they are derived. Phosphates which have previously existed in liquid manure are probably more soluble than the others. C. W. W.

Gases in the Tissues of Fruits. By A. Livache (*Compt. rend.*, lxxxv, 229—232).—The gases contained in the uninjured tissues of fresh fruits consist only of nitrogen and oxygen, in the same proportions as in atmospheric air. When the fruit has previously been crushed to a pulp, the oxygen is found a short time afterwards converted into carbonic acid, but existing in the same proportions to the nitrogen as before. Later, a real fermentative action succeeds the process of simple combustion, and the pulpy mass then disengages carbonic acid abundantly. Reference is made to *Compt. rend.*, lviii, 495; and lxxxiv, 1035. R. R.

Variegated Leaves. By A. H. Church (*Chem. News*, xxxvi, 237).—The white and green leaves of holly, maple, and ivy were submitted to examination, and it was found that the green leaves contain much more solid matter than the white leaves. In the ivy and holly nitrogen was more abundant in the white than in the green leaves, whereas with the ethereal extract containing wax, chlorophyll, &c., the opposite was the case. In the ash of the white parts potash abounds, while the ash of the green parts contains a considerable proportion of lime. A larger proportion of phosphorus is also present in the white than in the green leaves. E. W. P.

Comparative Chemical Examination of Thapsia Garganica, and Thapsia Silphium. By M. Yvon (*Pharm. J. Trans.* [3], viii, 162).—Admitting the identity of these plants, the author examined them, in order to ascertain whether the growth of the same plant in different latitudes affected its ultimate composition. The following results show that there is a considerable concordance between their mineral and organic constituents :—

	Organic.	Inorganic.	Starch.	Gum.	Gum resin.	Resin.
T. garganica	91·24	8·76	22·510	5·179	5·759	2·554
T. silphium......	90·26	9·74	26·124	5·421	4·271	3·192

Albumin.	CaO.	MgO.	Iron albumin.		Sulphuric acid.	Phosphoric acid.	Cl.	SiO_2.
1·354	1·365	0·677	·370	·224	·297	1·468	·219	2·715
0·624	1·368	0·697	·338	·508	·300	1·919	·420	0·707

The amount of resin is in both cases nearly the same, but the silphium resin was found to be more active, causing considerable discomfort to the nostrils, eyelids, &c., when its alcoholic solution was evaporated. Nothing of the kind occurred during the manipulation of the garganica resin. A. J. C.

Java Rhubarb. By Husemann (*Pharm. J. Trans.* [3], viii, 328).—Comparison is made between the physical characters and chemical constituents of the Chinese and Java rhubarb roots. Java rhubarb is said to be one fourth less active, and it is suggested that if chrysophanic acid be the active principle, then the inferior activity of the Java root depends upon the smaller quantity of chrysophanic acid present in it, and the activity might have been still further reduced, if it were not for the simultaneous diminution in the proportion of tannic acid, which by its antipurgative action, might act antagonistically to the chrysophanic acid. Schmidt's analysis shows the proportion of these two acids to be—

	Chinese root. per cent.	Java root. per cent.
Rheotannic acid	2·106	0·430
Chrysophanic acid	4·700	1·646

It is highly probable, in the author's opinion, that by cultivation, these two rhubarbs might be made to agree more closely.

A. J. C.

The Relative Value of Colchicum Root. By T. F. BECKERT (*Pharm. J. Trans.* [3], viii, 329).—The results of the comparative examination of the white, black, and grey varieties of colchicum root are said to indicate that the colour of the root is of no consequence, but that the age is of primary importance. A. J. C.

Analyses of Cotton Root-bark. By C. G. DRUEDING (*Pharm. J. Trans.* [3], viii, 245).—Five pounds of the bark were extracted with alcohol, and the solution was precipitated with acetate of lead, the bark residue from the alcoholic extraction being afterwards exhausted with water. The organic constituents thus obtained were a red and yellow resinous colouring matter, fixed oil, gum, sugar, tannin, and chlorophyll. The bark gave 6 per cent. of ash. A. J. C.

Products of Fermentation in the Refuse of Paris. By E. J. MAUMENÉ (*Compt. rend.*, lxxxv, 532).—A heap of fermenting refuse placed on the banks of the Seine for removal by boats was found by the author to give off no sulphuretted hydrogen, but carbonic acid and the vapour of ordinary alcohol were evolved, showing that the fermentation was alcoholic. This mass of refuse consisted chiefly of pea-pods, but those heaps which contained animal matter gave off carbonate and sulphide of ammonium and of compound-ammoniums.

R. R.

Analytical Chemistry.

Spectroscopical Notices. By HERMANN W. VOGEL (*Deut. Chem. Ges. Ber.*, x, 1428—1432).—This paper consists first of an account of a universal stand for use in examining flames, liquids, &c., by the pocket spectroscope. Secondly, the author shows that in detection of fuchsine in raspberry juice, the extraction with amyl alcohol should be preceded by the addition of a few drops of dilute nitric acid: for he finds that natural raspberry juice may give an amyl alcohol extract whose absorption spectrum resembles that of fuchsine in amyl alcohol. P. P. B.

Note on Mineral Analysis. By F. W. CLARKE (*Amer. Jour. Sci.*, xviii, 290).—In 1868 the author called attention to the fact that certain very refractory minerals are easily rendered soluble by fusion with a mixture of sodium fluoride and acid potassium sulphate. He now finds that in many cases the fluoride may be replaced by common salt, the mode of manipulation remaining the same. The finely pulverised mineral is mixed with 3 parts of the chloride in a capacious platinum crucible, and the mixture covered with 12 or 15 parts of the sulphate in small fragments. The fusion is then performed over an ordinary Bunsen flame, and is complete in five or six minutes. The fused mass, after cooling, detaches readily from the crucible and shows no trace of undecomposed assay.

This method is advantageously employed in cases in which the sulphate alone was formerly used. Chromite, treated in this way, furnishes a green mass completely soluble in hydrochloric acid, or the fused mass may be immediately treated with potassium chlorate and nitric acid, and the chromium oxidized by Storer and Pearson's method. It was not found possible to oxidize all the chromium in the course of the fusion. C. W. W.

Acidimetry. By A. HOUZEAU (*Compt. rend.*, lxxxv, 152—155).—The author proposes to use standard solutions of free ammonia for the estimation of acids in very dilute solutions. The ammoniacal solution is prepared by dissolving a known weight (5 to 50 milligrams) of ammonium chloride or sulphate in a litre of water, from which, after the addition of a little caustic potash (2 decigrams), 500 c.c. are distilled off. The distillate contains the whole of the ammonia of the salt employed, and forms an accurately standardised alkaline solution. R. R.

Estimation of Chlorine by Silver Nitrate and Potassium Bichromate in presence of other Salts. By H. PELLET (*Bull. Soc. Chim.* [2], xxviii, 68).—It is not necessary to separate arsenates, arsenites, phosphates, or fluorides, from a solution before determining the chlorine contained in it by the above method.

L. T. O'S.

Gravimetric Determination of Atmospheric Ozone. By A. LÉVY (*Compt. rend.*, lxxxv, 42—43).—In consequence of some remarks by Berthelot on the transformation of arsenious acid and sodium arsenite into arsenic acid and sodium arsenate by the influence of platinum, the author, who is daily examining atmospheric ozone by the change of potassium arsenite into arsenate, was led to investigate whether or not errors might occur in his determinations, as he is compelled in the process to employ metallic platinum. He gives his method of experimenting and a table of the determinations he has made; he finds that the influence exercised by the platinum on the potassium arsenite is not manifested in the circumstances under which he operates, and that the results obtained are not affected in an appreciable manner by any error due to the use of the platinum.

J. M. T.

Volumetric Estimation of Sulphuric Acid in Waters. By P. HAUBST (*Chem. News*, xxxvi, 227).—In waters for manufacturing purposes the sulphuric acid in combination with alkalis and earths is determined as follows:—A slight excess of baryta-water is added to 100 c.c. of the water, carbonic anhydride is then passed in, and the whole boiled and filtered. The filtrate, which contains the alkalis as carbonates, is titrated with a centinormal oxalic or sulphuric acid solution. To another portion sodium carbonate is added in excess; the sulphuric acid is then in combination with potash and soda, and the lime and magnesia are as carbonates. E. W. P.

Estimation of Free Sulphuric Acid in Vinegar, &c. By W. C. YOUNG (*Analyst*, Dec., 1877, p. 163).—30 c.c. are mixed with an excess of barium chloride; chlorine is determined in 10 c.c. by standard silver; the remaining 20 c.c. are evaporated to dryness; the residue is incinerated, and chlorine is again determined. The difference between the two determinations represents hydrochloric acid expelled by the free sulphuric acid. It is easy to calculate the amount of the latter from the data obtained. M. M. P. M.

Will and Varrentrapp's Method for determining Nitrogen. By C. MAKRIS (*Chem. Centr.*, 1877, p. 231).—Two sources of errors are found in this process. Ammonia is partially dissociated by passing over red-hot soda-lime; on passing air through the tube towards the close of the analysis, the ammonia is partially burnt. To do away with these errors the author proceeds as follows:—0·3 gram of pure sugar mixed with 20 times its weight of powdered soda-lime is placed in the posterior part of the tube; this is followed by a layer, 12 cm. long, of soda-lime in small pieces; then comes 3 cm. of powdered soda-lime; then a mixture of the substance under analysis with a little more than its own weight of pure sugar and with powdered soda-lime; then a layer of soda-lime in small pieces; and finally a plug of asbestos. The anterior layer of soda-lime is first heated to dull redness; then the layer coming after the mixed sugar and soda-lime at the posterior end of the tube; then the substance is heated so that a continuous stream of gas is maintained. As the evolution of gas slackens, the layer of mixed sugar and soda-lime is heated. The temperature should never rise above dull redness. M. M. P. M.

Some Remarks upon Sachsse and Kormann's Method for the Determination of Nitrogen when existing in Form of Amides. By E. SCHULZE (*Landw.-Versuchs Stat.*, xx, 117—123).—Sachsse and Kormann's method for the examination of amides, dependent on their behaviour with nitrous acid, does not always give satisfactory results. With asparagine, however, it answers well, the decomposition taking place thus:—

$$2(C_4H_8N_2O_3) + H_2O + N_2O_3 = 2(C_4H_6O_5) + 2NH_3 + 4N.$$

The results obtained by Sachsse with urea correspond partly with each of the two following equations:—

$$(1)\quad CH_4N_2O + N_2O_3 = CO_2 + 2H_2O + 4N.$$

$$(2)\quad 2(CH_4N_2O) + N_2O_3 = (NH_4)_2CO_3 + 4N + CO_2.$$

It is evident that when an amide of unknown composition is being examined, it is impossible to state whether nitrogen is given off from the nitrous acid itself as well as from the substance.

Nitrous acid acts like other mineral acids on asparagine, decomposing it into aspartic acid and ammonia, the last being converted into ammonium nitrite and remaining in the liquid: it is therefore only the nitrogen of the aspartic acid that is liberated, mixed with the nitrogen from the nitrous acid. As ammonium nitrite is converted into nitrogen and water by heat, it is probable that on treating asparagine, urea, &c., with nitrous acid, all the nitrogen would be liberated in the free state if the liquid were heated.

If we give to asparagine the formula $C_2H_3(NH_2)\left\{\begin{array}{l}CO.NH_2\\CO.OH\end{array}\right.$, we see that it is the NH_2 group connected with CO which is easily converted into ammonia, while the second NH_2-group, which replaces the hydrogen, resists more firmly the action of the acid. Urea, which has two $CONH_2$ groups, has a great tendency to form ammonia under the influence of acids. It is, therefore, highly probable that only such amides as are decomposed with production of ammonia by the action of strong mineral acids, undergo the same decomposition with nitrous acid as asparagine and urea: if this supposition be correct, it is easy to remove the uncertainty attending Sachsse and Kormann's process by boiling the amide with hydrochloric acid, neutralising the free acid with potash, and then treating with nitrous acid.

On boiling with hydrochloric acid, the NH_2 group above referred to, which is precarious in its behaviour with nitrous acid, is converted into ammonia; the other NH_2 group would most probably be decomposed with nitrous acid according to the ordinary equation, and the nitrogen could then be determined by dividing the total quantity obtained by 2: by then adding the nitrogen which has been converted into ammonia by boiling with hydrochloric acid to that already found, we obtain the total quantity present. With a view of testing the accuracy of this supposition, a mixture was made of asparagine and leucine dissolved in water; on treatment with nitrous acid, it gave a little less than the theoretical quantity of nitrogen; whereas, on boiling with hydrochloric acid, neutralising, and then treating with nitrous acid, it yielded just the quantity required by theory, as was to be expected. This amount divided by 2 gives the quantity of nitrogen in the form of amido-acids, aspartic, &c. R. C. W.

Note on Diphenylamine as a Test for Nitric and Nitrous Acids. By N. H. MARTIN (*Pharm. J. Trans.* [3], viii, 229).—The value of this test consists in its being readily used and its indications being quick and well-defined. Diphenylamine, about the size of a mustard-seed, is placed in a test-tube with a little sulphuric acid, and water is added to raise the temperature sufficiently to dissolve the diphenylamine. On adding the solution to be examined to that in the test-tube, a trace of nitric or nitrous acid is shown by a beautiful and very permanent blue coloration at the junction of the two liquids; if much nitric or nitrous acid be present, the colour is almost black.

One part of nitric acid (1·42) in 10,000, or 1 part of potassic nitrite in 30,000 parts of water, gives marked indications by this test.

A. J. C.

Tests for Carbolic and Nitric Acids. By DAVID LINDO (*Chem. News*, xxxvi, 155 and 180).—30 drops of a cooled mixture of sulphuric acid and water, 2 to 1 by measure, followed by addition of a few drops of nitric acid, give a red or pink colour with carbolic acid.

To detect traces of carbolic acid, it is better to use concentrated sulphuric acid, and to add a few drops of a solution of silver nitrate or mercurous nitrate. With mercurous nitrate, a bright yellow colour changing to brown and then to red, is produced.

A fresh solution of 5 grains carbolic acid to 1 ounce of water, serves as a test for nitric acid. 8 or 10 drops are mixed with 30 drops of concentrated sulphuric acid in a small basin, and a few drops of the liquid to be tested are added to the hot liquid, whereupon the red or pink colour above mentioned is produced. The test is tolerably delicate. Oxidising agents interfere with the reaction.

M. M. P. M.

Determination of Impurities in River and Well-water. By H. VOHL (*Deut. Chem. Ges. Ber.*, x, 1811—1817).—I. *Contamination of the Rhine Water between Cologne and Mühlheim.*—The steamers running between the above stations use the Rhine water for feeding their boilers, and on that account the boiler incrustations, as well as the last-formed concentrated residual water, are very suitable for determining the contamination of this river-water. The boilers are not fed with the condensed water, and no chemicals are used for preventing the incrustation. It is very difficult to give the quantity of water evaporated, and hence the quantitative results must be regarded as only approximate. The steamboat from which the objects of investigation were taken, had run between Cologne and Mühlheim uninterruptedly for three weeks, during which time the water was not blown off, nor the incrustation of the boiler removed. The water-mark of the Rhine was pretty high during this period.

Investigation of the Boiler-incrustation.—It formed a fine powder having a light-brown colour when dried. When heated it turned black, giving off a gas which burned with a bright flame, and had a disagreeable empyreumatic smell. It turned red litmus-paper blue and formed white clouds with acetic acid, indicating ammonia. 10 grams of the air-dried powder were dissolved in dilute hydrochloric acid with addition of potassium chlorate; the solution was filtered and treated with a few drops of sulphurous acid in order to destroy the free chlorine. After removing the excess of sulphurous acid by boiling, the cold solution was treated with sulphuretted hydrogen. The yellowish-white precipitate formed was filtered off, washed, and treated with ammonium carbonate. The filtrate was saturated with nitric acid, and evaporated to expel excess of nitric acid. A residue was thus obtained which gave a strongly acid solution when taken up with distilled water. A portion of this solution was treated with ammonium chloride, magnesium chloride, and excess of ammonia, which produced a white precipitate. The latter gave, by Marsh's test, a distinct arsenic mirror. The occurrence of arsenic in this water is no doubt due to the waste liquors from dye-works or aniline-colour works. Oxides of lead, copper, and zinc could not be found. For further examination, 10 grams of the dried powder were dissolved in hydrochloric acid and the solution was treated with sulphuretted hydrogen, filtered, and the filtrate evaporated to dryness. The residue was moistened with concentrated hydrochloric acid, again evaporated, and dissolved in distilled water with the addition of hydrochloric acid. By filtration, a considerable quantity of silicic acid was obtained. The filtrate was boiled with potassium chlorate in order to oxidize the iron present; it was next neutralized by ammonia and acidified with acetic acid. The light yellow precipitate formed was filtered off, digested with ammonium sulphide, the iron sulphide was collected on a filter, and the filtrate treated with magnesium chloride and ammonia after expelling the ammonium sulphide. A copious crystalline precipitate of ammonium-magnesium phosphate was at once produced. The filtrate from the ferric phosphate which had been acidified with acetic acid was treated with excess of oxalic acid, the calcium oxalate was filtered off, and the filtrate supersaturated with ammonia. A crystalline precipitate of ammonium-magnesium-phosphate was again obtained. The proportionately large quantity of phosphoric acid contained in the water is undoubtedly due to the fact that sewage-water passes into the Rhine.

100 grams of the powder dried at 100° were dissolved in hydrochloric acid, and the solution shaken with petroleum-ether. The ethereal solution left, on evaporation, small portions of oil, which solidified to crystalline masses and were easily saponified by alkalis, showing that fatty acids are present, due to waste liquors containing soap-water. The residue, insoluble in hydrochloric acid, mixed with sand and earth, showed under the microscope distinct fibres of wool, cotton, and wood.

Investigation of the concentrated residual Water.—The filtered residual water had a slight yellow colour, a very disagreeable bitter taste, and alkaline reaction. The water left, on evaporation, a strongly alkaline, brown residue, which turned black on ignition, with evolution of ammonia-vapours having a smell of burnt horn. Finally a yellow ash is left as residue. 10,000 parts of water gave 13·175 parts residue. The latter lost, on ignition, 2·480, so that 10·695 parts of mineral substances were left in the residue. Large quantities of chlorine, potash, and nitrates were found in the water, also sulphuretted hydrogen. These results show that the Rhine below Cologne is greatly contaminated with poisonous matter and substances injurious to health.

II. *Contamination of Well-water by Gas-liquor.*—The following circumstance is mentioned by the author. In Creuznach, several wells exist in the immediate neighbourhood of a gaswork, the water of which had been rendered impure by gas-liquor. The proprietor of these wells took out proceedings against the gasworks, but lost his case, inasmuch as certain chemists, who had examined these well-waters, were unable to detect in them the presence of compounds which are known to exist in gas-liquor; whereas a mixture of these waters with gas-liquor gave all the reactions which must necessarily be produced by the compounds present in gas-liquor. These chemists, however, had not noticed the changes which gas-liquors necessarily undergo when passing through the soil. It is a well-known fact that gas-liquor containing ammonium sulphide does not retain a trace of the latter after it has passed through a layer of earth only a few feet in thickness, and that the ammonia is combined as carbonate, sulphate, and thiosulphate. The empyreumatic substances present in gas-liquor are always retained by filtration through the soil. If the well is situated at a very great distance from the source of contamination, a portion of the ammonia may be converted into nitrous acid. The water in question was tested by the author, and gave results which proved that the water had been contaminated with gas-liquor passing through the soil into the well. Large quantities of ammonia, magnesia, nitrous acid, and thiosulphates were found. D. B.

Determination of Potash. By AD. CARNOT (*Compt. rend.*, lxxxiv, 1504—1507).—In a former paper it was pointed out that the reaction of the double thiosulphates of bismuth and the alkalis, or alkaline earths, might be used for the determination of potash, in presence of nitric or hydrochloric acid or of several bases, without previous separation. Since then experiments have shown that this method may be employed in presence of phosphates, iodides, bromides, cyanides, &c., the sulphates alone, in consequence of their insolubility in alcohol, presenting certain difficulties. This was a great objection to the process, as in a large number of cases in which potash has to be determined, sulphates are present. The author uses a solution of calcium thiosulphate, the composition of which, when crystallised, answers to $CaS_2O_3 + 6H_6O$; comparing this with the double thiosulphate to be produced, $Bi_2O_3.3S_2O_2 + 3(K_2O.S_2O_2) + 2H_2O$, it is seen that 3 equivalents of potash require 6 equivalents of lime. A slight excess of bismuth is necessary to prevent the decomposition of the lime salt. For the description of analytical details, reference must be made to the original paper. J. M. T.

Separation of Potassium and Sodium. By TH. SCHLOESSING (*Ann. Chim. Phys.* [5], xi, 561—570).—To a mixture of potassium and sodium salts ammonium perchlorate is added; on heating, ammonia and all volatile acids are expelled, leaving a mixture of perchlorates of potassium and sodium, which is washed several times with alcohol of 36°, in which sodium perchlorate is soluble. The residue of potassium perchlorate is, if necessary, dissolved in the smallest possible quantity of water, and the filtered solution evaporated to dryness, washed with alcohol, dried at 250°, and weighed.

The alcoholic solution of sodium perchlorate is evaporated to dryness, treated with sulphuric acid, and estimated as sulphate.

Non-volatile acids must be removed from the original solution.

The presence of the alkaline earths in no way impedes the separation. L. T. O'S.

Separation of Arsenic from Antimony by Bunsen's Method. By L. F. NILSON (*Zeitschr. f. Anal. Chem.*, xvi, 417—424).—According to the author, this method never yields trustworthy results; the error is to be traced to the employment of potassium thiosulphate, not to the sulphite. A very small trace of antimony may be detected in presence of arsenic, by adding a saturated solution of sulphurous acid to a solution of sodium thiosulphate, and boiling the liquid with a small portion of the substance under examination. If the liquid assumes a red colour with a bluish reflection, antimony is present.

M. M. P. M.

Arsenic in Tapers. By A. H. CHURCH (*Analyst*, Dec., 1877, 141).—Nearly one-third of a grain of As_2O_3 was found in each green taper weighing 16 grains. M. M. P. M.

Separation of Vanadic Acid from Alkalis.—By B. W. GERLAND (*Deut. Chem. Ges. Ber.*, x, 1216—1218).—The method of separation given in analytical text-books (which consists in precipitating the vanadic acid as insoluble ammonium-salt, by addition of ammonium chloride) is found by the author to be imperfect when potassium salts are present, inasmuch as the precipitate always contains a small quantity of potassium. Separation from sodium, however, is completely effected by this method.

Other compounds of vanadium resemble ammonium vanadate in carrying down and persistently retaining small quantities of potassium. In some cases ammonia is retained with the same persistency as potassium.

J. R.

Separation of Vanadic Acid from the Oxides of Aluminium and Iron. By A. BETTENDORFF (*Chem. Centr.*, 1877, 233).—Precipitate with ammonia and digest with ammonium phosphate. Iron or aluminium phosphate remains, while ammonium vanadate goes into solution. M. M. P. M.

Detection of Bismuth by von Kobell's Test. By W. M. HUTCHINGS (*Chem. News*, xxxvi, 249).—Cuprous iodide may be substituted for potassium iodide with advantage, as the mixture with sulphur does not deliquesce, neither is the sublimate of bismuth liable to be masked by a white sublimate, such as is given off when the potassium salt is used. An aluminium plate is preferable to one of porcelain or charcoal, as the faintest trace of the brownish-red bismuth is very conspicuous on it. E. W. P.

The Analysis of Tin Ores. By A. E. ARNOLD (*Chem. News*, xxxvi, 238).—Cassiterite, the principal ore of tin, is reduced in a current of hydrogen; a gram of the reduced substance is then caused to act on ferric chloride, and the amount of metal calculated by titration of the reduced chloride with permanganate solution. Or, when a complete analysis is required, the ore is first treated with hydrochloric acid or aqua regia, to remove the soluble gangue, the resulting dioxide being afterwards reduced by hydrogen, and dissolved in ferric chloride for titration, or in hydrochloric acid and potassium chlorate, for precipitation as hydrate or sulphide. E. W. P.

Precipitation of Manganese by Hydrogen Peroxide. By G. ROSENTHAL (*Chem. News*, xxxvi, 147—148).—On suspending recently precipitated hydrated manganese peroxide in water, and adding a solution of hydrogen peroxide, a brisk evolution of oxygen sets in, and by the addition of a little acetic acid, manganic oxide is dissolved, and may be separated by filtration; if sufficient hydrogen peroxide be used, the solution would become quite clear. If ammonia be added in presence of undecomposed hydrogen peroxide, the manganese goes down again as hydrated peroxide. This observation led to a series of experiments, with the view of estimating manganese by using hydrogen peroxide instead of bromine or chlorine. The result shows that manganese can be conveniently and accurately precipitated as peroxide after addition of a solution of hydrogen peroxide. In ores, slags, spiegeleisen, and ferro-manganese, the iron is separated from the solution of the chlorides by acetate of soda. The filtrate containing free acetic acid is boiled down to about 150 c.c., and allowed to cool. A solution of hydrogen peroxide (10 vols. commercially) is then added in the proportion of about 10 c.c. for every 0·1 or 0·15 gr. manganese in the liquid. After about an hour the liquid is to be neutralised with a few drops of dilute ammonia, when the manganese will go down in the form of black flocculent $MnO_2.H_2O$, while oxygen escapes. The mixture is heated gently, renewing the addition of ammonia carefully, until the excess of hydrogen peroxide is destroyed. The end of the operation, viz., total precipitation of manganese, is characterised by the separation of flocks, and by the supernatant liquid remaining clear. It is now filtered, washed with hot water by decantation, and finally on the filter, until the chlorine reaction disappears. The precipitate should be black. A large excess of hydrygen peroxide is to be avoided; much ammonium chloride is also objectionable. Where no iron is in solution, the manganese may be precipitated immediately after adding sodium acetate. The author gives some figures showing that the method is as accurate as any hitherto known, if not more so. One great advantage of his method is that no solids are brought into the solution with it, and that after the precipitation of iron, it is possible to work throughout with small volumes of liquid.

Riley has pointed out the difficulty of analysing manganiferous iron ores containing oxide of zinc and barium by the bromine method, these oxides going down with the manganese. From the author's experiments, however, it seems that the hydrogen peroxide method does not require a second precipitation of the manganese peroxide, as is the case with the bromine process. As regards oxide of calcium, the error caused by this base is insignificant when hydrogen peroxide is used. In working slags or ores rich in lime with bromine, serious mistakes must be made, in consequence of the excess of ammonia used, and of allowing the alkaline solution to stand.

In conclusion the author speaks against the necessity of the second precipitation of the iron, which has been more recently declared indispensable by Riley and by Stöckmann. D. B.

Volumetric Estimation of Manganese. By A. GARCIA PARVEÑO (*Ann. Chim. Phys.* [5], xi, 571—574).—The method described is a modification of Bunsen's method for the estimation of manganese dioxide, and differs from it only by the fact that the manganese is converted by heat into mangano-manganic oxide, Mn_3O_4, before treatment with hydrochloric acid. L. T. O'S.

Estimation of Manganese, Cobalt, Nickel, and Zinc by Precipitation as Oxalate. By A. CLASSEN (*Deut. Chem. Ges. Ber.*, x, 1315—1316).—The author has already described a process for determining manganese by precipitation as oxalate, found on the insolubility of manganese oxalate in concentrated acetic acid (*Zeit. Anal. Chem.*, xvi, 315). The same process has now been applied by him to the estimation of cobalt, nickel, and zinc. A neutral concentrated solution of the metallic salt is treated with potassium oxalate (1 : 6), and concentrated acetic acid added as long as a precipitate falls. The precipitate is warmed on a water-bath, collected on a filter, and washed with concentrated acetic acid or a mixture of equal volumes of concentrated acetic acid, alcohol (95 per cent.), and water. It is then ignited in the usual manner. E. N.

Separation of Iron from Manganese, Cobalt, Nickel, and Zinc. By A. CLASSEN (*Deut. Chem. Ges. Ber.*, x, 1316—1317).—The concentrated solution of the metallic salts is treated with a solution of potassium oxalate (1 : 6), and excess of strong acetic acid added. The oxalates of manganese, nickel, cobalt, and zinc are precipitated, leaving the iron in solution. The filtrate (and washings) is concentrated on the water-bath, rendered alkaline by sodium carbonate. The precipitate which forms is dissolved in concentrated oxalic acid, and the solution precipitated with acetic acid as before. The precipitate first obtained is washed with concentrated acetic acid, or a mixture of equal parts of acetic acid, alcohol, and water. It may still retain a trace of iron, which can be separated by a repetition of the process. E. N.

Estimation of Manganese, Nickel, Zinc, and Lead. By A. RICHE (*Compt. rend.*, lxxxv, 226—229).—The author precipitates manganese from its nitric or sulphuric acid solution by means of the current of one or more Bunsen elements. The platinum crucible containing the solution is made to form the positive pole, a coil of platinum wire the negative pole. During the operation the vessel is kept at a temperature between 70° and 90° on a water-bath. The presence of nickel, copper, zinc, magnesium, aluminium, earthy or alkaline salts, does not affect the operation, but a large proportion of iron must be avoided. The author claims for this method great accuracy and delicacy. When only one ten-millionth part of a gram of manganese is present, its existence is still revealed by the rose coloration which the current induces. The method has been successfully applied to demonstrate the existence of manganese in blood.

The paper describes methods of estimating nickel, zinc, and lead by electrical precipitation, which appears to offer great advantages for the analysis of alloys. Thus, it is stated that the analysis of a sample of brass can be made in a few hours, and lead may be directly estimated in presence of large proportions of silver, iron, zinc, nickel, cobalt, aluminium, or magnesium. R. R.

Separation of Nickel and Cobalt. By T. L. Phipson (*Chem. News*, xxxvi, 150).—The following method of detecting and isolating minute quantities of nickel in commercial chloride of cobalt said to be pure will give an idea of the practical nature of the new method which the author made known a short time ago:—A few grains of the above salt are dissolved in water, and the whole of the cobalt precipitated with the nickel by xanthate of potash, employed in slight excess and previously dissolved in distilled water. A few drops of ammonia are then added, and the dark green xanthate of cobalt collected on a filter. The nickel in the filtrate is precipitated by a few drops of ammonium sulphide.

Character of Xanthates.—Besides the yellow precipitate which the soluble xanthates give with salts of copper, all the insoluble xanthates, when dissolved in nitric acid, give rise to nitrous ether, easily detected by its odour. D. B.

Estimation of Nickel and Cobalt by Electrolysis. (*Dingl. Polyt. J.*, ccxxv, 65—67.)—Since the description of the estimation of copper by electrolytic deposition by the Mansfield Direction, in *Dingl. Polyt. J.*, 1865, clxxvii, 296; 1869, cxci, 147—285; cxcii, 50, 176; and 1875, ccxv, 440, with a description of a similar method for determining nickel and cobalt (*Zeitschr. für Anal. Chemie*, 1872, p. 1), the methods have been introduced only into the works at Mansfield and the Saxon Blue Works. Although the method for copper gives good results, Schweder, in the *Berg-und Hüttenmännische Zeitung*, 1877, pp. 5, 11, 31, and 40, has pointed out many objections. One is that the washing of the precipitated copper requires so much water, which has to be evaporated, that it is better to take a fresh sample, and after precipitating the copper in an acid solution by sulphuretted hydrogen, to treat the filtrate for nickel and cobalt.

The author gives several hints for avoiding the precipitation of the metals in form of small scales, which become lost in the washing. The chief points to be observed are to reduce the resistance of the fluid to the electric current by having the liquid charged with sulphate of ammonium, and to employ a comparatively strong current (a current that will decompose at least 200 c.c. of gas in one hour being recommended). Precipitation of oxide on the positive pole is to be avoided by saturation with ammonia. Avoidance of loss by spirting is obtained by use of a clock-glass, and attention is drawn to the error that may arise from the action of ammonia on the copper of the conducting wire.

Where much iron is present, Schweder recommends the following method. Copper is first separated, the residue is evaporated to dryness with nitric acid, and the excess of sulphuric acid is got rid of by heating. The residue is dissolved in 100 c.c. of hot water, allowed to cool, and 300 c.c. of cold water added, or, if much iron be not present, 200 c.c. will suffice. The solution is stirred, and a solution of carbonate of ammonium is allowed to drop gently in until the solution is dark brown, but with no trace of cloudiness. If this occurs, a little sulphuric acid is added. If the evaporation has been well carried out, little or no evolution of carbonic acid takes place on addition of the carbonate of ammonium. The solution is now boiled, whereupon the iron is precipitated. The precipitate is powdery, and can be easily washed. The solution is evaporated with a little acetate of ammonium until it can be put into the beaker for electrolysis. The precipitate is filtered off, sulphate of ammonium and ammonia added, and the nickel precipitated.

Wrightson (*Zeitschr. Anal. Chem.*, 1876, p. 297), says that nickel, cobalt, and copper can be precipitated from pure solutions, and easily determined. Solutions of nickel must not contain iron, and solutions of copper must be free from antimony. If copper and nickel only are present, the copper can be precipitated from a sulphuric acid solution, and then the nickel after addition of ammonia. Zinc can also be precipitated from an ammoniacal solution, and determined. S.

Separation of Iron, Chromium, and Uranium. By A. DITTE (*Ann. Chem. Phys.* [5], xii, 135—141).—This method is an extension of that of Deville for separating iron and aluminium (Wöhler, *Traité d'Analyse Chimique*, p. 131).

The mixture of sesquioxides of three metals obtained by precipitation with ammonia, after washing and ignition, is weighed in a porcelain boat, which is introduced into a porcelain tube and heated to redness in a current of hydrogen, giving a mixture of iron, uranous oxide, and chromic oxide. The iron is removed from this mixture by passing over it, whilst heated to redness, a current of hydrochloric acid gas. After cooling in a stream of hydrogen, the mixture of uranous oxide and chromic oxide is weighed. The uranous oxide is then dissolved out by nitric acid, leaving chromic oxide, which is washed, ignited, and weighed. The difference between these two weighings gives the uranous oxide, which is calculated as U_3O_4, and added to the weight of chromic oxide found. The sum of these deducted from the weight of the original mixture gives the weight of ferric oxide. The iron may also be determined directly by passing a current of steam mixed with a little hydrochloric acid through the tubes after the removal of the boat. The iron is carried along by the water which condenses, and in this liquor the iron may be estimated by the usual methods. The uranium may also be estimated directly from the nitric acid solution. By this method iron and chromium can be separated, as also iron and uranium, and uranium and chromium.

P. P. B.

Detection of Copper in Cast Iron, Steel, and Wrought Iron. (*Dingl. polyt. J.*, ccxxiv, 628—630).—Boussingault (*Ann. Chim. Phys.*

[5], v, 209) shows that in a solution containing iron and copper, if the iron be precipitated by ammonia, copper amounting to one fifty-thousandth only of the iron may be detected by nearly neutralising the solution with hydrochloric acid, and adding a drop of concentrated potassium ferrocyanide solution, a brownish-red precipitate or coloration being produced.

Since a little of the copper remains with the precipitated iron, Boussingault recommends that the copper should be precipitated by sulphuretted hydrogen from a hydrochloric acid solution of the iron, and weighed as sub-sulphide in estimating it quantitatively. The presence of arsenic does not interfere. J. T.

Analysis and Valuation of Spent Iron Oxides from Gas Works. By G. E. DAVIS (*Chem. News*, xxxvi, 188).—Water is determined by drying at 100°; the dried residue is digested with hot water, collected on a weighed filter, washed, dried at 100°, and weighed. In the filtrate ammonia is determined: it is calculated to sulphate. A portion of the washed residue is weighed into a porcelain boat, and then slowly burned in a stream of air, the products being passed into decinormal iodine solution.

Many analyses of spent oxides are given in the original.

M. M. P. M.

Estimation of Carbon in Iron and Steel. By ANDREW S. M'CREATH (*Dingl. Polyt. Jour.*, ccxxvi, 369—370).—The method generally adopted in the iron trade is the colorimetric method, in which the accuracy of the results depends on the exact determination of the carbon in the standard iron. The plan recommended by the author is a combination of the methods of Ullgren and Berzelius. It consists in dissolving the iron in a solution of chloride of copper and ammonium; with an excess of solution the precipitation of copper is avoided. The process is very rapid. 36 grams of double salt of copper and ammonium are dissolved in 120 c.c. of water, and 3 grams of iron or steel added. In 15 to 20 minutes the iron is dissolved and the solution is filtered through asbestos and carefully washed. Any basic chloride can be removed from the filter by further washing with the solution. The asbestos is placed in a flask with 3 grams of chromic acid and 10 c.c. water, and by the action of concentrated sulphuric acid carbonic anhydride is liberated, and after drying absorbed in potash-bulbs. The whole operation takes an hour. S.

Estimation of Phosphorus in Iron and Steel. By BOUSSINGAULT (*Chem. Centr.*, 1877, p. 236).—The method of estimation by means of cerium salts is not recommended by the author. Eggertz's molybdic method is good: a slight modification in the preliminary treatment of the iron or steel is described. M. M. P. M.

On the frequent occurrence of Cupric Acetate in Vinegar and on the Estmation of Copper. By ALFRED RICHE (*J. Pharm. Chim.* [4], xxvi, 23—28).—The author describes his examination of twelve samples of vinegar sold in Paris, seven of which contained copper in quantities varying from 5 to 15 milligrams per litre. The copper is probably derived from the brass taps and fittings of the vessels wherein the vinegar is stored by the retailer, and in many instances the presence of copper in preserved vegetables, &c., may be due to the use of vinegar containing copper. Several experiments were made to prove the rapidity with which brass or copper is attacked by vinegar.

The following method is recommended for the determination of copper in vinegar and such liquids:—

1st. In acid solutions. The nitric or sulphuric acid liquid is evaporated almost to dryness, then taken up with water. This solution is placed in a small platinum crucible which serves as the positive pole of a small Bunsen's battery, to which it is connected by a small bent piece of platinum foil dipping into the solution. The crucible is then heated to about 60° to 80° in water. By this method the author states that the whole of the copper was precipitated in a pure red condition when operating with pure salts of copper and with solutions containing small quantities of copper and large quantities of the salts of the alkalis and alkaline earths, of nickel, alumina, zinc, iron, manganese, and of lead.

Heat accelerates the deposition of the copper. 250 milligrams were completely precipitated in 1½ hours by the aid of heat, whilst 8 hours were required to obtain the full deposition in the cold.

In the presence of hydrochloric acid and chlorides it is preferable, for reasons stated by the author, either to expel these first by sulphuric or nitric acid, or to make the solution ammoniacal if this plan be expedient.

2nd. In ammoniacal solutions. The acid liquid is saturated with ammonia and submitted to the electric current. The action is slower but complete, 500 milligrams requiring 6 hours to be entirely precipitated. The precipitation is quickened by using two elements instead of one, but the copper is of a brown colour and does not present the fine red appearance as obtained in the other way described.

Vinegar can be at once subjected to the action of the current; but the black deposit on the platinum electrode must be dissolved in nitric acid and the solution taken to dryness. Water is added and the copper is precipitated in a pure and weighable form by again passing the current. In this manner, by operating on 75—100 c.c. of vingear, the whole of the copper is precipitated in about half an hour. A. J. C.

Detection of Zinc and Copper in the Human Body. By F. Raoult and H. Breton (*Compt. rend.*, lxxxv, 40—42).—As the presence of the above-mentioned substances in the human body, under ordinary circumstances, was pointed out some time ago, but nevertheless the question is still discussed by toxicologists, the authors have thought it advisable to publish the results of a judicial investigation made by them in 1874. From their experiments it appears that 500 grams of dry liquorice root furnished neither zinc nor copper. 400 grams of the intestines of a healthy man killed by accident gave no copper and only slight traces of zinc. 700 grams of the liver of a man who died in the hospital of Grenoble furnished 2 milligrams of copper and 7 milligrams of zinc. 400 grams of liver of a consumptive patient gave 6 milligrams of copper and 12 milligrams of zinc.

It appears, then, that the human body ordinarily contains copper and zinc, in quantities varying probably according to age, state of health, the nature of the food, and the kind of vessels in which it has been contained.

Hence it follows that to obtain chemical demonstration of poisoning by zinc or copper compounds, it is not sufficient to establish the mere presence of these metals in the body; but it must be further shown that the quantities found in a given weight of the incinerated substance are sensibly greater than the maximum quantity which might be found by similar means in an equal weight of substance obtained from the bodies of persons who had lived under similar conditions.

To prepare the animal matter for testing the authors proceed as follows:—The substance is carbonised with addition of a little sulphuric acid; the charcoal is heated to redness and in great part burned in contact with the air; and when the combustion becomes difficult in consequence of the softening of the residue, this residue is exhausted with a small quantity of nitric acid and water; the incineration is completed; the ashes treated with nitric acid; and the several liquors thus obtained are united and evaporated to dryness. The failure of certain toxicologists to detect copper and zinc in the body under ordinary circumstances is attributed by the authors to the neglect of proper precautions. They observe that copper especially remains obstinately fixed in the charred mass in spite of prolonged washing with hot nitric acid; and to reveal its presence it is necessary to incinerate the charcoal; and it is just this point which most experimenters appear to neglect. J. M. T.

Quantitative Analysis of a Mixture of Carbon Compounds. By R. Popper (*Zeitschr. f. Anal. Chem.*, xvi, 429—432).—From the estimation of carbon and hydrogen in a mixture, the author shows how the amount of each of three or four different compounds may be calculated. The method depends upon the solution of three or four equations with a corresponding number of unknown quantities.

M. M. P. M.

Determination of Carbon Sulphide, Copper Salts, and Caustic Alkalis by Xanthate of Potassium. By E. A. Grete (*Chem. News*, xxxvi, 156).—3·168 grams of copper sulphate are dissolved in water, Rochelle salt and sodium carbonate are added in excess, and the clear liquid is made up to 1 litre. Ammonia and caustic alkalis must be absent. 1 c.c. now = 0·01601 gram potassium xanthate and 0·0076 gram CS_2. The carbon disulphide is transformed into potassium xanthate, which is then determined by titration with the standard copper solution. The precipitate of copper xanthate readily settles upon agitation; the final point is known by the absence of turbidity on adding a drop of the copper solution. If a copper salt be dissolved in a mixture of Rochelle salts and sodium carbonate solution, and the liquid be titrated with standard potassium xanthate, the copper may be accurately determined. The standard xanthate liquid must be itself titrated against a standard copper liquid each time it is used.

Caustic alkali, even in presence of alkaline carbonates and sulphides, may be determined by dissolving the dried substance in absolute alcohol, adding carbon disulphide, precipitating all sulphide and sulphocarbonate by copper liquid (the final point is determined by the use of lead paper), and then completing the titration of the xanthate by means of the same copper liquid. Each Cu precipitated = 2KHO, or K_2O.

M. M. P. M.

Böttger's Sugar Test. By O. MASCHKE (*Zeitschr. f. Anal. Chem.*, xvi, 425—427).—The liquid—urine for instance—is decomposed by addition of tungstate of soda solution; to the filtered liquid a strong solution of soda is added and a small particle of basic bismuth nitrate; if a brown or black precipitate forms the liquid contains sodium sulphide. In such a case a fresh portion of the liquid is slightly acidified with acetic acid and a particle of basic bismuth nitrate is added; after standing a little time the liquid may be treated as already described. The prepared liquid is boiled for some time and then allowed to become perfectly cold. The presence of a trace of grape sugar is rendered apparent by the production of a black precipitate in the cold liquid. The tungstate of soda solution is prepared by dissolving 30 parts of crystallised sodium tungstate in 120 parts of water and adding 75 parts of acetic acid of 30 per cent.

M. M. P. M.

Determination of Alcohol in Ether and Chloroform. By A. H. ALLEN (*Analyst*, Oct. 1877, p. 97).—10 c.c. of the sample of ether are placed in a narrow test tube, a fragment of fuchsine is added, and the tube is corked. If there is no coloration, the ether is pure. If a coloration ensues, an equal volume of ether which has been treated with calcium chloride, and a fragment of fuchsine, are placed in a second similar tube. Alcohol is added in portions of one-tenth c.c. from a burette, until the tints are equal in both tubes. If the tints are not comparable, the tubes should be placed for a few moments in cold water. The alcohol should drop into the liquid, not on to the sides of the tube. Each one-tenth c.c. of alcohol added may be considered as showing 1 per cent. of alcohol present in the sample. The results are accurate within $\frac{1}{4}$ per cent.

The method could not be well applied to chloroform because of the difficulty of getting this liquid perfectly pure.

A modification of the common process for determining alcohol in ether is also described. A little fuchsine is shaken up with water, and a small quantity of ether in a glass-stoppered burette. Ether is insoluble in this liquid, but alcohol is dissolved by it. 10 c.c. are placed in a tube graduated in one-tenths of a c.c. 10 c.c. of the sample are added, and the tube is stoppered, and well shaken. When the ether rises to the surface, its volume is read off. Each 0·1 c.c. of reduction in volume = 1 per cent. of alcohol present in the sample. If the ether is coloured, the alcohol exceeds 20 per cent. In this case a fresh portion of the sample should be diluted with an equal bulk of pure ether, and the experiment repeated. The results are accurate to within 1 or 2 per cent.; they have been verified to 60 per cent. of alcohol.

M. M. P. M.

Manipulation of "Fatty Acids." By A. W. BLYTH (*Analyst*, Oct., 1877, p. 112).—A flask—300 to 400 c.c. capacity, with good stopper, carrying two tubes, one with stop-cock passing just through the stopper, the other passing nearly to the bottom of the flask, and bent externally like a syphon—is employed. After decomposition of the soap, the stopper is inserted, the flask inverted, the water drawn off by the short tube, and fresh water drawn up through the same tube, by sucking at the syphon. M. M. P. M.

The Detection of Adulterations of Oleum Theobromæ. By GUSTAVUS RAMSPERGER (*Pharm. J. Trans.* [3], vii, 772).—As the information given by writers on the above subject is somewhat meagre and uncertain, the author prepared pure cacao butter, from caracas beans by expression, and by extraction with ether and with carbon disulphide. The specific gravity test was then found to be useless, that of the first being 0·85, of the second 0·97, and that of the third being 0·958: the melting points of two specimens being 31—32°, and'of other 33—34°. Two parts of aniline or ether dissolve one part of the butter at the ordinary temperature, thus distinguishing and separating it from paraffin. Ether is, however, found to be the best test, as the solution of pure cacao-butter remains clear; but if wax, tallow, &c., are present, the solution become turbid, and deposits crystals on standing. The next most trustworthy test is that of taste, as when pure the butter melts quickly; and leaves no harsh taste, which is not the case if spermaceti, &c. is present. No sure test has been found to detect adulteration with beef marrow. E. W. P.

Separation of Salicylic Acid. By A. W. BLYTH (*Analyst*, Dec., 1877, p. 164).—The author prefers extraction by ether after addition of hydrochloric acid. In the case of milk, the liquid should be concentrated at 100°, then at 60° till pasty; the residue should be shaken with ether; after evaporation, the fat and salicylic acid may be readily separated. M. M. P. M.

Copaiba Testing. By L. SIEBOLD (*Pharm. J. Trans.* [3], viii, 250).—The only trustworthy method of testing copaiba is said to be the evaporation test. 1 to 1·5 gram of the sample is evaporated until all the oil has been expelled, when, in the absence of fatty oil, the resin is brittle and pulverisable. One per cent. of fatty oil diminishes the brittleness, and, with 3 to 5 per cent., the resin feels sticky. Castor and linseed oils may be distinguished by the odour when the resin is heated. By mixing the balsam under examination with pure Maranham balsam, in quantities varying from 10 to 50 volumes, it is easy to find in which the oil has been reduced below 1 per cent., and to calculate therefrom the percentage of adulterant. Small quantities of oil of turpentine can be detected by taking the boiling point of the sample, oil of copaiba boiling at 240—250°, and oil of turpentine at 160°. Also by distilling the suspected sample the presence of 2½ per cent. of oil of turpentine can be ascertained by the fact of its distilling over before the copaiba oil.

Gujgun oil is best detected by Hager's test. A. J. C.

Examination of Commercial Copaiba. By C. A. Bowman (*Pharm. J. Trans.* [3], viii, 330).—The author has not been successful in his endeavours to find a trustworthy test for the purity of the different varieties of copaiba, by which the presence of all adulterations could be detected. Petroleum-benzin properly applied will detect the presence of Venice turpentine, and will give very nearly the percentage of castor oil in the copaiba; *e.g.*

Paracopaiba was mixed with—

	30 per cent. Castor Oil.	20—50 per cent. Venice Turpentine.
Petroleum-benzin 1 to 4 parts.	Clear solution, even in presence of 2 of oil and 1 of copaiba.	Dense floccules, with 4 parts of turpentine.
Do., do., 10 to 12 parts..	Separation even with 10 per cent. oil.	Dense floccules, with 4 parts of turpentine.

The indications yielded by Para and Maracaibo copaiba and by Para copaiba mixed with—(1.) 30 per cent. castor oil; (2.) 30 per cent. linseed oil; (3.) 20—50 per cent. Venice turpentine, with absolute alcohol, and alcohol of ·817 and ·835 sp. gr., with ammonia, &c., are given in detail.

When evaporated, Para copaiba yields 44·4 per cent. of a hard resin and Maracaibo a plastic or soft residue. A. J. C.

On the Essential Oil of true Angustura Bark, By Oberlin and Schlagdenhauffen (*J. Pharm. Chim.* [4], xxvi, 130—133).—From 12 kilograms of bark, the authors have obtained 22·8 grams of essential oil, together with a viscid solid. After rectification over calcic chloride and redistillation on an oil bath, there remains in the retort a viscid mass, which is not volatile without decomposition, and is equal to about one-tenth of the weight of the oil taken. The oil distils at 267°. It is colourless, and has a density equal to ·934; the specific rotatory power = + 5·4°. It possesses an aromatic odour, resembling that of the bitter orange rind (*Aurantii cortex*).

Iodine has no action on it in the cold, but at water-bath heat it yields a green mass, with disengagement of hydriodic acid. Bromine attacks it violently, the mixture passing, as the solution becomes saturated with bromine, into a viscid mass, and changing from blue to purple and brown; at the same time large quantities of hydrobromic acid are evolved. On cooling, after expelling excess of bromine, there remains a firm brittle mass, which is fusible at steam heat. Its composition has yet to be determined. Ether, petroleum spirit, and bisulphide of carbon dissolve it, but it is insoluble in alcohol. It is soluble in nitric acid, but is precipitated from the solution by water. Chlorine also attacks it energetically, but its substitution-products have still to be studied. Strong acids attack it more or less. Nitric acid, hydrochloric, chromic, and iodic acid, the two last acids on the addition of alcohol, produce in each case a rose-coloured compound.

Ferric chloride, in presence of ether, gives a fine carmine coloration, which is very evanescent.

An alcoholic solution of cupric chloride yields a cherry-red colour.

The authors have examined Brazil Angustura bark, *Esenbeekia febrifuga*, but do not find in it any evidence of an essential oil.

A. J. C.

Laboratory Notes on Quinine. By A. B. PRESCOTT (*Pharm. J. Trans.* [3], viii, 407).—*The Solubility of Quinine (precipitated by Ammonia or Soda Hydrate) in Water-washing.*—0·25 gram of quinine sulphate was precipitated by caustic soda, and the alkaloïd washed on the filter, until the filtrate gave no reaction with barium chloride. The loss was 11·6 per cent. of the alkaloïd. In another experiment, the same result ensued with ammonia as the precipitant. Allowing 24 hours to elapse after precipitation, and washing the precipitates on the filter with 18·4 c.c. of water, the soda precipitate lost 2·9 per cent. of the alkaloïd, and the ammonia precipitate 10·6 per cent.

·28 gram of dried quinine lost 50 per cent. of its weight when washed with 500 c.c. of water at 87° F.; each c.c. of water dissolved ·000216 gram alkaloïd.

A solution of sodium sulphate has practically neither more nor less solvent power than pure water.

For quantitative work the precipitation of quinine as alkaloïd is inaccurate under any circumstances.

Gravimetric Determination of Quinine as a Precipitate by Potassiomercuric Iodide.—The reagent can be prepared by adding potassium iodide to mercuric chloride. The value of this precipitate washed and dried at 212° F., equals 2·9 grams for 1 gram of quinine dried at the same temperature. It bears washing without a weighable loss.

Determination by precipitating with Acid Solution of Sodium Phosphomolybdate.—This precipitate is exceedingly close, and bears washing without loss, but cannot be dried above 70° C. 3·665 grams of this precipitate equal 1 gram of quinine dried at 100°.

Solubility of Quinine in Ether.—20 parts of washed ether dissolved 1 part of quinine monohydrate, after 24 hours' digestion in a stoppered vessel.

Citrate of Iron and Quinine.—Six samples examined were found to contain 5·2, 12·2, 8·7, 9·0, 11·4, 8·3 per cent. of alkaloïd. Sulphates were present in each sample, and the author discusses the futility of separating the sulphate from the alkaloïd, with a loss of the latter, as is the case when the pharmacopœia method is followed in making this preparation. A. J. C.

Note upon a Reaction of Emetine. By F. B. POWER (*Pharm. J. Trans.* [3], viii, 344).—A trace of emetine brought into contact with chlorinated lime, preferably acidified with a weak acid to liberate the hypochlorous acid, gives a bright orange or lemon-yellow coloration. A few drops of a solution of 1 part of emetine to 1000 parts of water, when evaporated to dryness, readily produce the coloration, and the colour is still perceptible with a solution containing 1 part of the alkaloïd in 5000 parts of water. The reaction is recommended to be employed as a means of detecting emetine in forensic analysis, and of testing the value of the various species of ipecacuanha. Emetine can be very easily isolated from complicated organic substances by amylic alcohol, chloroform, benzene, and petroleum-benzin in an alkaline solution. By this test the author confirms the supposition which has been already entertained, of the absence of emetine in *Richardsonia scabra.* A. J. C.

Chemico-legal Determination of Hyoscyamus niger, Datura Stramonium, and Atropa Belladonna. By S. WASILEWSKY (*Chem. Centr.*, 1877, p. 9).—The author employs Dragendorff's method. 720 grams of the leaves are cut up and mixed with flour and fat, treated with water, and acidified with hydrochloric acid. The mixture is heated for 24 hours at 50° and pressed, the residue again treated in the same manner, and the liquors are evaporated on a water-bath to a thin syrup, which is treated with three times its volume of alcohol, and filtered after 24 hours' standing. After removing the alcohol from the filtrate by distillation, the aqueous residues were shaken with petroleum ether, until the latter remained colourless, then rendered alkaline by means of ammonia, warmed, and extracted twice with benzene. After evaporating the benzene at 50°, belladonna and datura stramonium left a slight residue of white colour; hyoscyamus a yellowish amorphous residue, weighing 0·006 gram; belladonna, 0·005 gram; and datura stramonium, 0·003 gram. Since ether extracts only a very small quantity of alkaloïd, the aqueous liquids were, after warming and acidifying, treated with chloroform, rendered alkaline, and finally shaken up with chloroform three times. The evaporated residues of the chloroform was recrystallised twice, and dried; *Hyoscyamus* gave 0·108 gram of amorphous mass; *Datura stramonium,* 0·376 gram of yellow crystals; and *Atropa belladonna,* 0·410 gram yellow crystals. Chloroform, however, appeared to dissolve about 0·002 gram of alkaloïd, when it was used for purifying the acid liquids, while ether, petroleum ether, amyl alcohol, and benzene did not take up the alkaloïd; the former cannot therefore be used for this purpose. D. B.

Extraction of Copper by means of an Acid Solution of Ferrous Chloride. By A. HAUCH (*Chem. Centr.*, 1877, 10, 11).—For extracting copper from malachite, hydrochloric acid was used. The author, however, made it his object to diminish the use of this solvent as much as possible. By treating the hydrochloric extraction-liquor with metallic iron, in order to precipitate copper, a liquor is obtained, which contains ferrous chloride. By mixing carbonate of copper with the correspondingly concentrated liquor of ferrous chloride, we obtain ferric oxide, ferric chloride, and cuprous chloride, the latter of which is insoluble in the resulting liquor. By adding a corresponding quantity of hydrochloric acid, the cuprous chloride is converted into cupric chloride, which dissolves in the liquor, and from which the copper is thrown down by iron. The same result is obtained by using common salt instead of hydrochloric acid. The solution of ferrous chloride must have a density of at least 14° B., and must be used in excess, as malachite ores contain other carbonates besides that of copper. The extraction is performed at the ordinary temperature, in wooden tanks or vats provided with agitators. D. B.

On the Artificial Colouring of Wines and the means of Detecting the Fraud. By E. J. Arm. Gautier (*J. Pharm. Chim.* [4], xxv, 8—12, and 102—106).—The following reactions should be tried with strongly clarified wines, as was shown at the head of the table in a preceding paper (*Chem. Soc. J.*, 1876, ii, 438).

Pernambuco or Brazil-wood.—Wines coloured with these substances are not decolorised, even after being clarified with two or three times as much albumin as is indicated in the table (*loc. cit.*); they assume a yellowish colour, which changes to a fine red in the air. The reactions with sodium carbonate, ammonia, borax, alum, and sodium carbonate are very sensitive. If a small piece of silk, thoroughly cleansed from gum (dressed), be washed with dilute tartaric acid, and soaked in the wine for 20 to 24 hours, and then dried at 60—70°, it will appear of a distinctly maroon or reddish-lilac colour, whilst in the case of an unadulterated wine it will remain wine-coloured, or lilac. If silk thus dyed by wine coloured with Brazil wood be then soaked in dilute ammonia, it will become reddish-lilac, whilst the silk dyed in the pure wine will change to dark grey, with scarcely a trace of the original colour. If lime-water is substituted for ammonia, the silk from the adulterated wine will become greyish, that from pure wine of a dingy yellowish-red colour. If the coloured silk be soaked in aluminium acetate solution, and then heated to 100°, it will retain its wine-red lilac colour, a reaction which distinguishes wine thus coloured from that coloured with Brazil wood. Brazil and logwood are not employed to any extent in the countries where wine is largely produced.

Logwood.—If the colour due to logwood is in excess in the wine, ammonia imparts a violet tint to it. Wine coloured with logwood imparts to silk, which has been treated as described above, a reddish or maroon-lilac colour, which is changed to a violet-lilac tint by dilute ammonia, and to a bluish-violet by aluminium acetate.

Cochineal.—The change to rose colour on addition of 10 per cent. alum solution is characteristic. Sodium carbonate imparts a lilac-brown colour, but entirely destroys the vinous or red colour due to *Phytolacca.* If a piece of dressed silk be mordanted with aluminium acetate, and immersed for 20 hours in the wine, and then dried at 100°, the colour imparted is violet wine-red, very like that given by pure wine. It does not change colour with copper acetate (showing absence of fuchsine); if soaked in a dilute solution of zinc chloride, heated to 100°, washed with sodium carbonate, then with water, and dried, it assumes a purple colour, whilst with pure wine it remains of a dull, lilac-grey. The absorption-bands of cochineal cannot be distinguished with certainty until more than 12 per cent. of the total colour of the wine is due to cochineal. Cochineal is rapidly precipitated in the lees of the wine.

Fuchsine.—Aniline colours are so extensively used for wine-colouring, that they should be looked for even after the detection of other colouring substances. Fortunately they are easily detected by adding ammonia, shaking with ether, and adding acetic acid to the partly evaporated ether solution, when a rose or violet-red colour is produced.

To detect mere traces of fuchsine by this test, the ammonia must be added in quantity more than sufficient to saturate the wine, and gentle heat must be applied. Faure states that there is a yellow colouring matter in wine, which produces a solution in ether, at first colourless, but becoming red and at last violet on exposure to air and light: hence the preceding processes must be carried out as rapidly as possible.

Another process for detecting fuchsine consists in separating the fuchsine by means of amylic alcohol from the liquid obtained by adding subacetate of lead to the wine and filtering. Yvon separates the colouring matter by shaking the wine with animal charcoal, filtering, washing the charcoal with water, and then extracting the colouring matter by alcohol; the colouring matter is entirely removed from 10 grams of wine by 1 gram of charcoal.

Wine coloured with fuchsine imparts a rose colour to the "dressed" silk, pure wine giving a more violet tint. The former becomes yellow when treated with hydrochloric acid, and reddish-violet if dried at 100°; after having been treated with dilute copper acetate solutions, the silk dyed with pure wine becomes bright rose with the acid, and greyish-violet by treatment with copper acetate and drying at 100°.

Arsenic should always be looked for in wines containing aniline colours. Fuchsine is rapidly precipitated from all wines when they are kept.

Phytolacca.—This fraud is less frequent than it was several years ago. The reddish or lilac colorations given by aqueous solutions of sodium carbonate or borax, or better still by sodium bicarbonate, are very sensitive. The lake obtained by adding alum and sodium carbonate assumes a violet tint when the coloration due to phytolacca amounts to 25 per cent. of the total colour-intensity of the wine. Duclaux finds that nascent hydrogen decolorises wine falsified by phytolacca; the author succeeded in decolorising a diluted wine containing phytolacca in 24 hours, by zinc and hydrochloric acid. The colorations imparted by fuchsine and cochineal are also decolorised by nascent hydrogen, although more slowly.

Althaea Nigra or Mauve Noire.—The petals and entire blossoms of althaea are often used; they impart a perceptible flavour to the wine, followed after several months by a disagreeable taste, whilst the colour quickly separates. Aluminium acetate gives a distinctly bluish colour. Pasteur, Balard, and Wurtz propose pouring into 1 c.c. of the suspected wine, which has been diluted to a rose tint, four or five drops of very dilute sodium aluminate solution; a violet colour is then obtained, which, however, also results from wine coloured with elder, danewort, or whortleberry. These adulterations are distinguished by putting into 1 or 2 c.c. of the wine a small crystal of ferrous sulphate, and adding several drops of an aqueous solution of bromine; pure wine becomes yellowish; if it is adulterated with "mauve noire," the colour becomes bright violet; elder becomes intense blue, and danewort becomes dull yellow. On dissolving a crystal of iron alum in infusion of the "mauve" of elder and of danewort, the "mauve" becomes yellow without precipitating; the elder precipitates and the liquid becomes green; with whortle and danewort a deposit also forms, but the coloration is brown; with pure wine also a precipitate forms, but the colour of the liquid is less brown than in the preceding case. These last methods of distinction are insufficient, but further means are described below.

Red Beet.—The beet is generally employed only for masking certain mixtures, since by itself it loses much of its colour during fermentation, and quickly passes to red or brown. If fresh it becomes lilac with solution of sodium bicarbonate charged with carbonic acid, and changes to yellow with alkalis, if old.

Elder- or Danewort-berries.—These berries ars used to colour light white wines; the danewort always imparts a faint disagreeable turpentine smell. In Spain and Portugal these berries are used to give a peculiar colour and taste to sweet and very alcoholic wines. The *teinte de Fismes* is made by digesting elderberries in alum solution, and submitting them to pressure. As much as 4 to 7 grams of alum per litre have been found in wine thus adulterated, and alum should always be looked for if the above colouring substances are found. Wines coloured with the berries give a deep blue violet-lake with alum and sodium carbonate. This test is very characteristic, especially if made comparatively with the pure wine. The ammonia, sodium aluminate, and sodium acetate reactions are not recommended. If a piece of flannel or silk be mordanted with aluminium acetate, and be heated with 20 grams of wine until this is almost evaporated, and the flannel or silk be then washed and placed in some water containing a few drops of ammonia, its colour changes to green if it has been in pure wine; to deep brown if in wine coloured with elder, and probably also if coloured with danewort.

Privet-berries.—Privet is little used for colouring wine in France. Its violet-red colour fades gradually, especially if the berry has fermented, and then imparts only a much less rich red colour. If present in wine, its colour becomes blue or green by alkalis and alkali-carbonates; green or grey by bicarbonates; but borax does not change its colour.

Whortleberries.—This colouring matter is scarcely met with in French wines. In the table (*loc. cit.*) (*Chem. Soc. J.*, 1876, ii, 438), the principal characteristics of this colouring matter are given. Citric acid should always be looked for if whortleberry colouring is suspected, and its detection is one of the best proofs of this adulteration.

Indigo.—Reaction (A. c.) and (B. b.) in the table (*loc. cit.*) is sufficiently sensitive to indicate indigo by itself; the smallest traces can be found. 50 c.c. of the wine are usually sufficient for the experiment.

A piece of silk or wool mordanted with aluminium acetate, and heated nearly to dryness with 20 to 40 c.c. of the wine, washed, and soaked in dilute ammonia, becomes dull green if the wine was pure, and blue if it contained any indigo sulphate. The formation of chloraniline as a test for indigo is of theoretical rather than practical value. Such indigo is often added only to tone down bright colours, as fuchsine and cochineal. Other colouring matters should always be looked for in the wine after removing the indigo in the fining. Indigo disappears very rapidly in wines artificially coloured; hence when the wine itself is found free from indigo, the lees, after having been washed with water, often give when boiled with alcohol, the coloration characteristic of indigo. F. C.

Detection of Foreign Colouring Matters in Red Wine. By HILGER (*Dingl. polyt. J.*, cxxv, 310).—Genuine red wine treated with caustic lime becomes brown, or dirty bluish-grey, gradually changing to brown. Occasionally a greenish colour appears momentarily. Whortleberry juice on caustic lime becomes deep blue, then gradually green; madder instantly becomes green; the juice of Phytolacca berries becomes yellow, and fuchsine becomes colourless. A piece of chalk moistened with the wine, if genuine, becomes brown or slate-grey; if the wine is coloured the stain becomes, in presence of whortle-

	Hydrogen (Zn & HCl).	$(NH_4)HO$.	KHO conc.	$CuSO_4$.	Amyl Alcohol.
Madder	Decolorised after short time	Green, passing to yellow	Brown	Intense blue	Dissolves much colouring matter on shaking, with red colour.
Kermes-berry (Phytolacca)	Decolorised after 12 hours	Yellow	Yellow	Dark-brown, becoming green	No trace of colouring matter dissolved.
Whortleberry juice	Decolorised very slowly, 12 to 24 hours	First violet, passing to red, and lastly to brown		Splendid violet	Takes up almost all colouring matter with intense colour.
Fuschine....	Decolorised instantly	Decolorised	Decolorised	—	The same.
Genuine wine	Decolorised after a time	Becomes gradually brown	As with $(NH_4)HO$	Slowly becomes brown	Takes up a little colouring matter, becoming red.

berry, blue to violet; with mallow, blue or green; with Phytolacca berries and fuchsine, no change.

The table (p. 938) may be used to confirm the results obtained.

New red wine is quickly decolorised by nascent hydrogen; old wine very slowly. J. T.

Detection of Magenta in Wine. By L. LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 866).—By means of the absorption-spectrum 1 in 500,000 can be detected. C. S.

Detection of Glycerin in Wine. By E. REICHARDT (*Arch. Pharm.* [3], x, 408).—Pure wine contains from 6 to 8 grams of glycerin per litre; adulterated wine may contain from 1 to 3 litres of glycerin per 100 litres.

Slaked lime is added, in slight excess, to the wine extract, the mass is boiled with alcohol (90 p. c.), and the filtrate is evaporated on the water-bath. The glycerin remains nearly pure. M. M. P. M.

Estimation of the Dried Extracts of Wine. By E. HONDART (*Bull. Soc. Chim.* [2], xxviii, 59—62).—The author explains that there exists a certain relation between the density of a wine and the weights of water, alcohol, and extract which it contains; and upon this relation he bases two methods for the determination of the extract.

(1) The alcohol is distilled from the wine, and the residue filled up with distilled water to its original volume; the density of the liquid is then taken to three places of decimals, the last two of which multiplied by 2·25 give the weight of the extract. As this method requires great practice before accurate results can be obtained, the following, which is of greater practical use, has been devised:—

(2.) The alcoholic strength of the wine is ascertained by means of Gay-Lussac's tables. The density of the wine is taken with a baroneometer (an instrument constructed for the purpose by the author), and the difference between the two densities is multiplied by 2·06, which gives the weight of the extract. L. T. O'S.

Detection of Wines sophisticated with Grape Sugar. By C. NEUBAUER (*Dingl. polyt. J.*, ccxxv, 309).—White wines are examined directly in a Wild's polaristrobometer, with a sodium light, for right-handed polarisation. For red wines 100 c.c. are evaporated to 50 c.c., treated with pure animal charcoal, filtered, and diluted to 100 c.c. This is then examined optically if colourless; if not the wine is treated first with lead acetate, then, if necessary, with charcoal as before. The following results were obtained:—

	I.	II.
Alcohol	7·85 p. c.	6·66
Free acid	1·99	0·50
Sugar	0·59	0·895
Right-handed rotation	0·0	6·4°

I is a pure white wine of 1874; II is a wine to which sugar has been added.

Neubauer recommends a simple, cheap, and satisfactory optical wine-tester, made by W. Stug, of Homburg. J. T.

Salt in Beer. By J. W. GATEHOUSE (*Analyst*, Nov., 1877, p. 130).—From his own analyses, and from the analyses of others, the author regards 3·35 grains of salt per gallon of beer as a fair average quantity to be set down as due to the hops used. To find the salt due to malt alone, he gives the following formula:—

$$\frac{\text{Original gravity of wort} - 1{,}000}{100} \times 6{\cdot}6 = \text{grains of salt per gallon.}$$

If to these two amounts the quantity of salt in the water used be added, we have a maximum number, any salt over and above which must have been fraudulently added. M. M. P. M.

Analysis of Blood-ash. By A. JARISCH (*Chem. Centr.*, 1877, 7).—The only novelty in these analyses is the direct carbonisation of the blood in a porcelain crucible over a naked flame. The author regards the objection which Hoppe-Seyler formerly had to the use of porcelain vessels as untenable, since he has proved that by carbonising sugar with phosphate of sodium the ash contained merely 0·0025 silicic acid. As a mean, the following composition of the ash was obtained:—

	Man affected with Pneumonia.	Man (normal).	Horse.	Cow.	Dog (normal).	Dog (feverish).
Phosphoric anhydride	8·16	8·82	8·38	4·98	12·74	12·73
Sulphuric „	11·44	7·11	6·31	6·17	4·13	3·76
Chlorine	28·63	30·74	28·63	35·12	32·47	33·32
Potash	22·92	26·55	29·48	10·74	3·96	3·11
Soda	26·06	24·11	21·15	37·44	43·40	44·69
Lime	1·24	0·9	1·08	1·15	1·29	1·14
Magnesia	0·52	0·53	0·60	0·18	0·68	0·40
Ferric oxide	7·03	0·16	9·52	9·24	8·64	8·35
CO_2	—	—	1·30	2·97	—	—

D. B.

Estimation of Matter precipitated from Milk by Rennet. By L. MANETTI and G. MUSSO (*Zeitschr. Anal. Chem.*, xvi, 402—406).—The authors adduce reasons for preferring, for the purpose of the cheese manufacturer, an estimation of the amount of precipitate caused by addition of rennet, to that of the precipitate caused by acetic acid. The milk should be of the same degree of acidity as it possesses before being used for cheese making. If too acid, carbonate of sodium must be added. A glycerine solution of rennet is added to 50 grams of the milk; the temperature is maintained at 35° to 40° for some time; the precipitate is collected on a filter, washed well with water, then with ether and with hot alcohol, dried at 115°, and weighed. Further details are given in the original.

M. M. P. M.

An Error in the Estimation of Fat in Milk and in Milk Products. By L. MANETTI and G. MUSSO (*Zeitschr. Anal. Chem.*, xvi, 397—402).—The hot ethereal extract of milk solids contains globules of a dark colour, heavier than, and immiscible with melted fat. These globules are darkened and partially resinised on heating, and are at the same time rendered insoluble in ether. This substance is insoluble in carbon disulphide: it is believed by the authors to be lactic acid. M. M. P. M.

Estimation of Nitrogen in Milk, &c. By G. MUSSO (*Zeitschr. Anal. Chem.*, xvi, 406—417).—The author burns the milk with soda-lime, using special precautions, and employing special forms of apparatus, detailed in the original. M. M. P. M.

Milk Analysis. By J. CARTER BELL (*Analyst*, December, 1877, 155).—183 samples of genuine milk were personally collected. The following are the average results from each dairy:—

No.	Cows.	Total solids.	Solids not fat.	Fat.	Ash.
1.	20	13·6	10·0	3·6	0·80
2.	25	12·7	9·6	3·1	0·77
3.	11	13·5	10·1	3·4	0·75
4.	20	13·5	9·8	3·7	0·77
5.	2	12·6	9·2	3·4	0·71
6.	19	13·5	9·8	3·7	0·73
7.	3	15·2	10·5	4·7	0·81
8.	5	13·0	9·6	3·4	0·73
9.	5	13·1	9·9	3·2	0·79
10.	6	12·7	9·4	3·3	0·75
11.	4	13·7	9·3	4·4	0·76
12.	6	14·2	10·0	4·2	0·73
13.	6	14·8	11·3	3·4	0·78
14.	16	13·2	9·4	3·8	0·70
15.	2	13·5	10·1	3·4	0·79
16.	25	13·7	10·1	3·5	0·78
17.	8	13·7	9·9	3·8	0·77

The author insists upon the expediency of determining ash: the amount does not fall below 0·68 per cent. in genuine milk. Experiments conducted by the author show the falseness of the idea that milk drawn from a large supply late in the day is likely to show lower results on analysis than milk drawn early. M. M. P. M.

Technical Chemistry.

On certain Photographic Processes. By ALPH. POITEVIN (*Ann. Chim. Phys.* [5], x, 525—541).—The author gives historical sketches and working details of photographic processes based (1) upon the action of light upon certain organic substances in presence of potassium bichromate.

(*a.*) A given surface is prepared by applying a solution of gelatin in the aqueous bichromate: on exposure to light in a camera, those portions which are acted upon lose the property of swelling up under the influence of cold water. A bath of the latter, therefore, develops an image in relief. This is hardened by immersion in a solution of ferrous sulphate, and is then reproduced in plaster casts, from which the image may be transferred to copper plates by the usual electrochemical methods; or a metallic coating may be deposited upon the original surface, previously rendered conducting. The reliefs thus obtained are employed in typographic printing. It is found advantageous to prepare the surface with gelatin simply, and to sensitize just previous to use by immersion in a saturated solution of the bichromate; crystallisation of the latter on the prepared plates is avoided by the addition of a small quantity of a saturated solution of alloxantin to the bath.

(*b.*) Photographic impressions for printing in inks are obtained upon surfaces similarly prepared with albumin and bichromate. After exposure, a transfer-ink is applied by means of a roller; this is resisted by those portions which have been protected from the action of the light, and *vice versâ.*

The image thus obtained is then transferred to the stone for printing.

(*c.*) Direct impressions are obtained upon lithographic stones by applying to their surface a small quantity of the gelatin solution, and printing upon them by means of light from the negatives prepared as above. After exposure they are washed with glycerin, and the image developed by applying a roller charged with transfer-ink and varnish.

The image is etched by means of a dilute acid.

(*d.*) Permanent photographs in carbon are obtained by incorporating this body in a finely divided condition with the solution of gelatin and bichromate. Surfaces are prepared with this as before by exposure in the camera, those parts acted upon by the light become insoluble, while those which are not acted upon remain soluble, and are removed by treatment with warm water.

The author gives details of the methods by which he fixes the image thus developed, and transfers it when desired to other surfaces.

(*e.*) Short descriptions are given of the photographic methods based upon the modification produced by the action of light upon a surface previously prepared with a solution of 11 pts. ferric chloride and 5 pts. tartaric acid in 100 pts. water. The action in question consists in the reduction of ferric to ferrous chloride. Water is condensed upon those parts of the surface which have been acted upon, by reason of the deliquescent properties of the latter compound, in quantity proportionate to the degree of the action. Any pigment in a fine state of division, when dusted over such a surface, will be retained by the hygroscopic portions, and develop an accurate reproduction of the object to be photographed.

Impressions on glass, developed by means of vitrifiable pigments or metallic oxides, may be further developed in a permanent form by exposure to the heat of a muffle.

Photographic impressions on enamels may be similarly obtained, the process being somewhat modified to suit the special requirements of the case. C. F. C.

On the best Means of Utilising the Waste Water obtained in the Manufacture of Potato-starch. (*Dingl. polyt. J.*, ccxxv, 394—396.)—The waste water from these manufactures has to be purified on account of the complaints against its passage into streams and rivers. Gaultier de Claubry (1837, lxiii, 465; 1841, lxxx, 399) precipitates with milk of lime and tan solution (Lohabkochung), and uses the product for manure. Markt (1874, ccxiv, 225) precipitates with lime. Other proposals are these (1838, lxviii, 406):—Neutralise with soda or lime and evaporate, or precipitate with soda and alum. Burggraf (1835, lvi, 464) made researches on the irrigation of meadows and arable land with this refuse water, and with good results, and Märcker (*Zeits. des landwirthschaftlichen Centralverens der Provinz Sachsen*, 1876, 7) also gives results of experiments in this direction.

According to Schulze and Märcker potatoes contain:—

		Sol. in water.
Moisture	76·69	—
Starch	15·40	—
Nitrogenous matter	1·63	1·02
Woody matter	0·90	—
Other organic substances	4·51	—
Mineral matter	0·87	0·84

And good potatoes contain even 1·20 per cent. of nitrogenous, and 1·08 per cent. of inorganic matter soluble in water. 1,000 tons of potatoes contain 6·52 tons of soluble potash, 1·87 of soluble phosphoric acid, and 1·90 tons of soluble nitrogen.

The starch manufactory at Hohenziatz treated 1,216 tons of potatoes for starch between 4th October, 1874, and 6th February, 1875. The waste water, after passing through precipitating vats, &c., for the purpose of collecting all the particles of starch, was conducted into a reservoir and mixed with spring water. This water was conducted over a meadow of 18·5 acres, and then passed to a meadow of 4·95 acres, and from this to the third and last, which contained 6·19 acres. The 29·64 acres received the water from 1,064 tons of potatoes, or for each acre 4·38 cwt. of potash, 1·26 cwt. of phosphoric acid, and 1·27 of nitrogen.

The following table shows analyses (1) of potato-water; (2) of the same diluted; (3) of water from first meadow; (4) water from second meadow; 1 litre contained:—

	1. mg.	2. mg.	3. mg.	4. mg.
Whole solid matter ..	1857·8	323·8	322·8	262·0
Organic matter......	1134·2	101·8	38·0	78·8
Inorganic „	723·8	222·0	348·8	183·2
Potash	212·5	55·0	41·2	8·2
Phosphoric acid	56·6	5·5	trace	trace
Nitrogen	140·7	12·0	4·0	9·1
Ammonia	37·4	0	0	0
Nitric acid	3·8	trace	trace	trace

The disappearance of ammonia and phosphoric acid in (2) is accounted for by the precipitation of phosphate of magnesium and ammonium on the addition of the spring water. The harvest in hay before the use of potato-water was 19·13 cwt. per acre, and afterwards 31·88 cwt.* The composition of the hay after is better than before:—

	1.	2.
Moisture........................	15·00	15·00
Woody matter	22·66	22·82
Mineral matter..................	7·64	8·69
Sol. in ether	2·00	2·30
Albumin........................	10·89	15·85
Extractable matter not containing nitrogen......................	41·81	35·34
	100·00	100·00

S.

Conditions which should be fulfilled by Water for Domestic Use. By F. FISCHER (*Chem. Centr.*, 1877, 264, 280, and 300).—An historical summary of the results of different authors and workers.

M. M. P. M.

Denitrification of Nitrous Sulphuric Acid by Sulphurous Acid. By G. LUNGE (*Deut. Chem. Ges. Ber.*, x, 1432—1440).—This paper contains an account of experiments undertaken to show the inadmissibility of the experiments of Kuhlmann (Hofmann's *Bericht über die Entw. der Chem. Ind.*, i, 174) and of Vorster (*Dingler's Journ.*, ccxiii, 411—506) to explain the action which takes place in a Glover's tower; both these investigators claim that nitrous oxide and nitrogen are formed. The author in his mode of experiment approaches as nearly as possible to the chamber process, by passing measured volumes of SO_2 and air through a known quantity of nitrous sulphuric acid heated to 200° (somewhat higher than the temperature of a Glover's tower). The gases are then led into a large glass balloon containing diluted pure sulphuric acid, whence they pass through a series of absorption-tubes, the first of which contains pure sulphuric acid, and the last a known volume of semi-normal solution of potassium permanganate, and, finally, to control the exit of N_2O_3 or NO_1 through starch-paste solution containing potassium iodide. The amounts of N_2O_3 contained in the nitrous-sulphuric acid, and that set free in the large balloon, and the portion absorbed by the sulphuric acid and permanganate of potash in the tubes, are determined by titrating with a semi-normal solution of permanganate; a method first used by the author for this purpose (*Deut. Chem. Ges. Ber.*, x, 1074).

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* This yield is not large. Two cuttings in England generally yield from 46 to 50 cwt., and I have known cases higher than this.—S.

From a series of experiments, the author concludes that in presence of excess of air, as in the Glover's tower, no reduction of NO or N_2O_3 to N_2O or N takes place. He also shows that when pure SO_2 is passed through nitrous sulphuric acid heated to 110—130°, and the NO formed is oxidised by allowing air to enter, no loss as N_2O or N is to be observed. Finally, by passing the gas through heated porcelain tubes, he finds that in presence of excess of oxygen, SO_2 is unable to reduce N_2O_3 to N_2O and a portion to nitrogen. P. P. B.

Direct Preparation of Soda and Potash from their Chlorides.

By E. Bohlig (*Dingl. Polyt. J.*, ccxxiv, 621—623).—Magnesium oxalate, produced in a subsequent process, is mixed with equivalent quantities of sodium chloride and hydrochloric acid in the cold. Acid sodium oxalate immediately separates out thus:—

$$MgC_2O_4 + HCl + NaCl = NaHC_2O_4 + MgCl_2.$$

The washed sodium oxalate is treated with water, and an equivalent amount of magnesium carbonate is agitated in an air-tight vessel. When the pressure, which increases at first, has subsided, sodium bicarbonate remains in solution and magnesium oxalate is precipitated. The bicarbonate boiled with magnesia, obtained subsequently, yields sodium carbonate and magnesium carbonate. The acid magnesium chloride solution is evaporated, and heated in a soda furnace. Part of the resulting magnesia is taken to neutralise a fresh quantity of magnesium chloride solution, and of the other part, after washing to remove chloride, half is added to the sodium bicarbonate solution as above, and the other half is treated with CO_2 to form carbonate.

The oxalic acid is obtained by heating pine-wood sawdust with potash-lye.

Potash may be produced directly from potassium chloride by the same method. J. T.

Resistance of Aluminium to Atmospheric and other Action.

By Clemens Winkler (*Dingl. polyt. J.*, ccxxvi, 70—75).—Hitherto aluminium has been considered to be a metal easily attacked by the atmosphere, and by weak alkalis and acids. This idea has prevented its employment to any great extent, and yet zinc, which is quite as easily attacked, is one of the most useful metals in the arts. To thoroughly test the resistance of this metal to the wear and tear of ordinary daily use, the author had three spoons made; one of silver, one of German silver, and one of aluminium. From the 1st of February, 1876, for a whole year, these spoons were daily used for all purposes, gravies, soups, &c. They were each cleaned to the same extent and in the same way, by first wiping with flannel and soap, and then dipping into warm, and afterwards into cold water. Now and then, they were washed in a weak soda-solution. After a time the aluminium spoon lost its brightness, assumed a greyish-blue appearance, and showed signs of mechanical wearing. The German silver became dull and greenish in appearance. The silver lost its lustre, but kept its whiteness. Both the silver and German silver spoons showed less signs of mechanical wearing than the aluminium. The following table shows the loss at each weighing:—

Spoon of—	Date.	Weight.	Wear.		Wear in 1 year per cent.	Average yearly wear.
			Days.	Per cent.		
		grams.				
Aluminium....	1876. 1 Feb.	25·493	201	0·200	0·360	0·630
„	„ 20 Aug.	25·442				
„	„ 12 Oct.	25·428	53	0·055	0·378	
„	1877. 26 Jan.	25·343	106	0·334	1·150*	
German silver..	1876. 1 Feb.	53·616	201	0·370	0·643	1·006
„ ..	„ 20 Aug.	53·417				
„ ..	„ 12 Oct.	53·335	53	0·153	1·054	
„ ..	1877. 26 Jan.	53·130	106	0·384	1·322	
Silver	1876. 1 Feb.	44·148	201	0·203	0·368	0·403
„	„ 20 Aug.	44·058				
„	„ 12 Oct.	44·033	53	0·057	0·390	
„	1877. 26 Jan.	43·974	106	0·133	0·457	

From this it can be seen that aluminium wears better than German silver, and nearly as well as silver.

The author instituted experiments on objects in aluminium exposed to atmospheric action. A storm destroyed these objects, however, and the experiments will have to be repeated. The writer publishes the above experiments in answer to a criticism by Karmarsch (1877, ccxviii, 16) on the proposal to use aluminium for coinage. While not believing that aluminium is suitable for money purposes, he adduces the following as a proof of its resistance to ordinary wear and tear. In 1873 he had some medals struck in this metal, and, though exposed since that time to the action of air in his laboratory, they are as bright as ever. The same is the case with some coins. He hopes that the value of this metal may become better known, and the range of its use thereby extended. S.

Manufacture of Alabaster-, Milk-, Bone-, Cryolite-, and Opal-Glass. By M. Hock (*Dingl. polyt. J.*, ccxxiv, 623—628).—The chief constituents of *alabaster-glass* are non-ferruginous sand and potash. The presence of sodium salts in the potash should be avoided, as they tend to produce transparent easily fusible glass. Most recipes include "burnt bones," but good alabaster glass can be produced without them. Borax increases the lustre and fusibility of the glass, but is not absolutely necessary. Powdered talc is much to be recommended. Good results are obtained by taking 100 parts sand, 40 parts potash containing at least 95 per cent. of carbonate, 5 borax, and 5 talc.

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* Probably cleaned too much.

The potash may be reduced to 30 parts if a hot regenerative gas furnace be used. Coloured glasses are obtained by adding, for turquoise, copper oxide and sulphate, or copper oxide with a little nitre; and for chrysoprase, uranium oxide with a little copper oxide. A fashionable grey-violet colour is obtained by adding manganese oxide and Ceylonese graphite.

Milk- or *bone-glass* is obtained by adding sufficient bone-ash or tin oxide. Of late bone-ash has often been replaced by burnt guano:—

(*a*) 100	parts	sand.	(*b*) 100	parts	sand.
30	„	bone-ash.	35	„	potash.
30	„	potash.	30	„	burnt guano.
5	„	borax.	3	„	nitre.
5	„	minium.	3	„	tin oxide.

Cryolite is now applied in Bohemian works to imitate imperfectly French and Belgian opal-glasses. The effect of cryolite depends mainly on its alumina. The fluorine, however, acts prejudicially on account of the volatile compound formed with silica. Too much cryolite renders the glass too opaque, and the fluorine injures the pots and furnace. The following mixture yields a good glass:—100 parts sand, 20 parts cryolite, 12 parts soda, 4 parts sodium nitrate, 2 parts zinc or lead-oxide.

An analysis of Belgian opal-glass gave:—

SiO_2.	PbO.	FeO.	Al_2O_3.	K_2O.
63·7	16·5	0·3	16·8	2·3 = 99·6

Here the alumina gives opacity, whilst the large quantity of lead oxide tends to the durability of the finished objects. Experiment shows that 100 parts of finely powdered felspar free from iron, and 22 of minium free from iron and copper, form a completely homogeneous, fusible mass, easily worked without decomposition. This glass in its properties closely approximates to the French and Belgian glass. Metallic oxides yield very rich colours with it. J. T.

Desilverisation of Lead. (*Dingl. polyt. J.*, ccxxxv, 67—70; and Stoddart, in *Engineering*, September 15th, 1876).—After a brief reference to Parker's process, and the difficulties it presents in a manufacturing point of view, and a few remarks on Flach's improvements, the author describes a method adopted at Glasgow, and known as the Flach-Guillim process. 18 tons of rich lead are melted, and 1 per cent. of zinc added. The molten mass is then allowed to cool. The crust which forms is removed, and the lead sweated out in a small pot. The lead in the large pot is then treated with another ½ per cent. of zinc in the same way. A third addition of ¼ per cent. of zinc suffices to remove the greater part of the remaining silver, 5 dwts. being left, in the lead per ton. This lead is then run into the improving pan, and the last traces of zinc oxidized out.

The zinc and silver alloy is heated in a plumbago crucible with a luted cover. A plumbago pipe leads to a cast-iron receiver. A coke fire is used. The zinc distils over, and is again used. The silver and lead alloy is then cupelled.

All the oxide of lead formed in the operation is reduced in a slag hearth, the fumes being condensed in Johnstone's patent condenser. The lead from the slag hearth, being very impure, has to be treated in an improving pan, by which the impurities are removed. The purified lead is then desilverised as before. Lead by this process can be desilverised in 30 hours with a loss of 1¼ per cent. The market lead contains only ·0015 per cent. of antimony, and ·0004 per cent. of silver.

S.

White Lead. By G. W. WIGNER and R. H. HARLAND (*Dingl. polyt. J.*, ccxxvi, 82—85).—The value of white lead depends on its covering-power or body, *i.e.*, on its opacity. The Dutch process, which yields 90 per cent. of the total quantity manufactured, affords a paint best answering to these requirements. The authors think that white lead is a mere mixture of neutral carbonate and hydrate in proportion of 3 of the former to 1 of the latter, each retaining its chemical properties. Their experiments show that the hydrate forms a varnish which will cover a surface, but which is not opaque. Carbonate with oil forms an emulsion, sufficiently opaque, it is true, but with no power of covering a surface. Together in the above proportions, the results were highly satisfactory. S.

Note on a White Lead Coloured Yellow by Oil. By FRED. WEIL and FERD. JEAN. (*Bull. Soc. Chim.* [2], xxviii, 5—6).—A sample of white lead, prepared by the Dutch method, when mixed with oil, was coloured yellow in the interior, whilst the surface remained white. This is due to the fact that the white lead contained excess of oxide which, in contact with the air, absorbed carbonic acid, forming the carbonate, and in the interior a lead soap was formed, which gave the mass a yellow colour. L. T. O'S.

Products of Combustion of Coal-gas. By C. HEISCH, W. C. YOUNG, and G. W. WIGNER (*Analyst*, Nov., 1877, pp. 133, 135, and 138).—These are three independent papers. In the first the author found the atmosphere of a small badly-ventilated room in which coal-gas was burned, to be free from sulphurous acid: by cooling the atmosphere and examining the moisture condensed, he found 0·3 grain H_2SO_4 per 100 cb. ft. of gas burned: the gas contained 20 grains of sulphur per 100 cb. ft. In a similar experiment with a gas containing 5·5 grains of sulphur per 100 cb. ft., he found only ·056 grain H_2SO_4. The production of sulphuric acid, therefore, increases more rapidly than the actual increase in amount of sulphur. The air coming from a gas-referee's apparatus without ammonia-salts was found to contain sulphurous acid, this was oxidised at a very short distance from the orifice of the eduction-tube.

In the second paper the presence of sulphuric acid in the atmosphere of a very well-ventilated room is proved by numerous experiments. Moist linen and paper, cards, &c., were placed in different positions in the room; these were washed after the combustion had proceeded for a measured time, and sulphuric acid was determined in the washings. Dust from old books, from furniture, &c., was examined: dust from apartments in which coal-gas was never burned, was also examined. In every case strong evidence was found in support of the statement that the greater part, if not the whole, of the sulphur in the gas is converted, in combustion, into sulphuric acid.

A deposit which formed on the inner surface of the chimney of a "Sugg's London Argand," was found to be stannic sulphate: hence sulphuric acid was produced close to the base of a flame where combustion is supposed to be but partially complete.

In the third paper, experiments are described carried out in an artificially-ventilated room in which the escaping air was cooled and tested. No sulphurous acid was found. In the worst experiments, 22 per cent. of the total sulphur present, and in the best experiments, 62 of the total sulphur were recovered as sulphuric acid.

M. M. P. M.

Cost of Lighting and Heating by Petroleum and Gas. (*Chem. Centr.*, 1877, 238—39.)—At present, petroleum is as cheap a source of light as gas: as a heating-agent, petroleum, taken at the average price, is about three times more costly than gas. M. M. P. M.

Destruction of Leather by Gas. By A. H. CHURCH (*Chem. News*, xxx, 179).—The backs of books from a large library were scraped, and 6·21 per cent. of free sulphuric and 2·21 per cent. of combined acid were found present. M. M. P. M.

Utilisation of the Gases issuing from Metallurgical Hearths. By L. CAILLETET (*Compt. rend.*, lxxxv, 955—957).—The gases issuing from metallurgical furnaces contain a sufficient quantity of combustible principles to render it possible to use them as fuel, and owing to the large quantity of carbon monoxide, they may be used as reducing agents. L. T. O'S.

A New Process for the Preparation of Extracts without Heat. By A. HERRERA (*Pharm. J. Trans.* [3], viii, 283).—For the concentration of vegetable juices, and in general of aqueous solutions of organic principles, the author finds that, on congealing these solutions, the dissolved principles remain in the mother-liquors, and that two or three congelations are generally sufficient to produce a solution concentrated enough to allow of the extracts being finished either by exposure to the sun, or in the drying-closet. The congelation is performed in a freezing-machine (sorbetière), with a freezing-mixture of ice and either sodic or calcic chloride. After a large portion of the solution has congealed, the ice-mass is pressed, and the mother-liquor congealed a sufficient number of times, just short of the precipitation of any sparingly soluble principles. Extracts so prepared are said to represent accurately the properties of the plants, which is not always the case with those which are obtained by heat-concentration. For example, conium-extract prepared in this way has th[illegible] characteristic odour of conine, and when dissolved in water represents the juice of the plant in appearance and properties, its albumin being unaltered. This method is recommended for—(1.) The preparation of aqueous extracts in general; (2.) Of syrups containing juices, in which case the concentration should be carried so far, that after mixing with the simple syrup, the requisite density is obtained; (3.) For the conservation of juices; (4.) For chemical analysis. A. J. C.

New Method for the Extraction of Resin of Scammony. By PERRET (*Bull. Soc. Chim.* [2], xxviii, 522—523).—Powdered scammony is treated with boiling alcohol, and the solution exactly neutralised with sulphuric acid; a lake compound of the colouring matter and the aluminium and calcium contained in the resin separates out; the solution is filtered and evaporated, and the residue dried at 104°, whereby a very pure resin is obtained. L. T. O'S.

The Application of Nitroalizarin to Steam Dyeing. By L. STAMM (*Dingl. polyt. Jour.*, ccxxiv, 643—644; *Bulletin de Mulhouse*, 1877, p. 22).—The author has obtained a reddish-orange on cotton, which appears fully only after soaping, whilst after washing with water only, it appears somewhat dull. Sufficient acetic acid to prevent the formation of a lake is added to the dye before use. A little calcium acetate increases the brightness of the shade, whilst excess diminishes it. The intensity of the colour increases up to a certain point with the amount of alumina mordant used, and then begins to diminish. Aluminium nitrate as mordant gives a darker reddish, and less pure orange than the acetate. The following mixtures give the best results:—

Nitroalizarin	1·0	l.
Acetic acid	0·5	„
Calcium acetate (s.g. 1·141)	0·1	„
Aluminium acetate (s.g. 1·115) ..	0·25	„

or—

Nitroalizarin	1·0	l.
Acetic acid	0·5	„
Calcium acetate	0·15	„
Aluminium nitrate (s.g. 1·16)	0·25	„

The addition of 150—200 grams of potassium ferricyanide to either of these gives a brown; double the quantity of ferricyanide gives a colour almost black, which becomes brown after soaping.

0·5—0·6 chromium oxide, added to 1 litre of nitroalizarin gives with ferricyanide a brown, varying in shade with the amount of the latter taken.

A finished piece steeped for twelve hours in a basic chloride of lime solution of sp. gr. 1·0431 was scarcely changed. The bath acts injuriously on the orange only wh[illegible] acid is added. J. T.

Vanadium Aniline-black. By G. WITZ (*Ding. polyt. Jour.* ccxxiv, 639—642; *Bulletin de Mulhouse,* 1876, p. 425).—Experiments made on a large scale show that 1 litre of colour containing

80 grams of aniline chloride and 1·3 m.g. vanadium give the black colour on cotton in two to three days when the two thermometers of the hygrometer stand at 20° and 25°. The cost of the vanadium method is less than that of the copper-sulphide method. The vanadium compounds of the alkalis, being not very soluble in water, are dissolved in dilute hydrochloric acid, reduced with glycerin, and made up to a strength of 10 grams of metallic vanadium per litre. With concentrated dyes the more aniline is present, the less vanadium is required. If 90 grams of aniline chloride be taken above the vanadium may be diminished by 25 per cent. in amount. The formation of the colour may be accelerated by increasing or retarded by diminishing the quantity of vanadium added. When copper sulphide is used, gum, dextrin, and burnt starch cannot be used as thickening materials, but with vanadium they may be used for certain patterns if the vanadium be increased about twenty-fold. Methyl-violet, 0·3 gram to a litre of colour, is used to blend with the black. Vanadium-black gives, on being steamed after oxidation, a beautiful black without tendency to become green. J. T.

Method of preventing Aniline-black from turning Green. By JEANMAIRE (*Dingl. polyt. J.*, ccxxiv, 448—449).—Ordinary aniline-black, as printed on cotton, consists, according to recent views (*Dingl. polyt. J.*, ccxxiii, 640) of two black colouring matters; one being unaltered by acids, the other forming with alkalis or neutral compounds a bluish-black, which acid liquids or gases convert into a green.

This blue-black, which is the essential cause of aniline-blacks turning green, is converted into the former unaltered variety of aniline-black by acid oxidising liquids, such as bichromate of potash, chromic acid, or by the oxygen-compounds of chlorine.

The author recommends (*Bulletin de Mulhouse*, 1876, 494, and 1877, 47) the use of acid ferric sulphate for oxidising this emeraldine-black. Commercial ferric sulphate is treated with one or one and a-half times its weight of common sulphuric acid, and the mixture is introduced into a standard colouring bath containing 1 or 2 grams of iron to one litre of water; 6 to 8 pieces require 1 to 2 litres of this solution. The aniline-black pieces, before passing through the finishing process, are placed in the former bath and oxidised at 75° to 80° for about an hour, after which they are soaped or merely washed.

To prepare the salt, 20 kilos. of ferric sulphate are dissolved in 60—70 litres of water and treated with 5 kilos. of bichromate of potassium and 15 to 18 litres of common sulphuric acid. For 6 to 8 pieces 4 to 8 litres of this mixture are required.

For aniline-black orange, chromic acid is required, using for 6 to 8 pieces 300 to 400 grams; *i.e.*, 300 or 400 grams of bichromate of potassium and 0·25 litre of sulphuric acid.

Since free chromic acid destroys indigo-blue, the above receipt has to be altered slightly for the solid-blue of aniline-black, 4 kilos. of potassium bichromate being used for the above quantity instead of 5. D. B.

Use of Quebracho as a Dye-stuff. By J. ARNADON (*Bull. Soc. Chim.* [2], xxviii, 524—527).—Quebracho contains a very fine yellow colouring matter which, under the influence of light, changes to orange, and may be fixed on certain fabrics, especially on wool, as follows:—The wool is mordanted with spirits of tin and cream of tartar, and dyed in a decoction of the wood at a temperature of 80°.

Other woods used in tannin possess similar dyeing purposes.

L. T. O'S.

Albumin of Commerce. By C. T. KINGZETT and M. ZINGLER (*Pharm. J. Trans.* [3], viii, 253).—None of the plans hitherto adopted are competent to produce albumin from blood at all comparable in value with egg-albumin. The authors' process yields a solution of albumin from blood which will keep during the hottest weather without the slightest decomposition, and is as white as egg-albumin. Blood, either crude or defibrinated by whipping, but preferably the prepared serum, is placed in a suitable apparatus with 5 per cent. of turpentine. For two to ten hours a current of heated air is rapidly blown through the mixture until the bleaching action is completed. After having settled, the albumin solution is siphoned off from any residual oil and passed through grey filter paper. Albumin so prepared is somewhat analogous to ordinary forms of albumin, but has the additional advantages of gelatinising entirely when heated and of presenting an albumin-solution which does not putrefy. It possesses other advantages specified by the authors.

This process depends upon the formation of peroxide of hydrogen, camphoric acid, and other bodies, by the aërial oxidation of turpentine, as described by one of the authors in previous papers. A. J. C.

Analyses of Preserved Vegetables. By J. ATTFIELD (*Pharm. J. Trans.* [3], viii, 236).—In the preservation of vegetable substances probably little actual chemical alteration takes place if the perfectly sound vegetable be at once rapidly desiccated at a low temperature, although the question may arise, does desiccation, or other mode of preservation, so physically alter constituents not chemically altered, as to impair the value of the vegetable substance, either as food or as medicine? The results of the analyses, which are given in detail, of the preserved vegetables, taken from the residual store of the ships of the late Arctic expedition, show that—(1) the carrots and potatoes were of good quality. (2) The cabbage was deficient in mineral matter, especially in alkaline phosphate, and the cause is ascribed to the possible loss of vegetable juice in the pressing of the fresh vegetables before they were dried. (3) The mixed vegetables were also deficient in saline substances, possibly from the same cause.

A. J. C.

Utilisation of Wine-lees. By P. MULLER (*Bull. Soc. Chim.* [2], xxviii, 58, 59).—The lees or dregs of common wines, generally used for the preparation of potash, and as manure, may also be utilised for the preparation of tartaric acid. The dregs are allowed to ferment, pressed out, and dried in the air; then treated with hydrochloric acid, which dissolves the cream of tartar; to the filtered solution is added milk of lime. Tartrate of lime decomposed by sulphuric acid yields the free acid. L. T. O'S.

Composition of Bohemian Wines. By J. Hanamann (*Dingl. polyt. J.*, cxxv, 311).—The following table gives the average composition deduced from 40 samples, of wines of the years 1868—75:—

Year.	Alcohol, weight.	Alcohol, volume.	Acid.	Extract.	Ash.
	Per cent.		Weight per cent.		
White wines.					
1868	10·74	13·31	0·607	2·01	0·133
1872	10·09	12·48	0·652	2·04	0·150
1874	9·83	12·16	0·624	1·96	0·149
1875	9·51	11·78	0·556	1·99	0·156
1873	8·65	10·72	0·563	1·95	0·177
Mean	9·76	12·09	0·60	1·99	0·15
Red wines.					
1868	9·96	12·34	0·614	2·24	0·218
1872	9·37	11·61	0·548	2·16	0·215
1874	9·36	11·58	0·515	2·15	0·212
1875	8·84	10·95	0·571	2·20	0·242
1873	7·50	9·31	0·562	2·31	0·226
Mean	9·00	11·16	0·56	2·21	0·22

The amount of sugar did not exceed 0·2 per cent. J. T.

Composition of an Ancient Wine. By M. Berthelot (*Ann. Chim. Phys.* [5], xii, 407—412).—This wine, which is between 1500 and 1600 years old, consists of a yellow liquid, and a solid matter held in suspension. On analysis, the liquid gave the following results per litre:—Alcohol, 45 c.c.; combined acids, 3·6 grams; potassium bitartrate, 0·6 gram; acetic acid, 1·2 gram; traces of tartrate of lime and acetic ether. L. T. O'S.

Beer Analyses. By C. Reischauer (*Deut. Chem. Ges. Ber.*, x, 1341, 1342).—I. Salvator of 1874. II. Ditto of 1875. III. Ditto of 1876. IV. Draught beer from Zacherl. V. Lambic from the brewery of Emile Becquet, Brussels, 1869. VI. Beer from Bufe, of Heligoland.

	I.	II.	III.	IV.	V.	VI.
Sp. gr. of the Beer......	1·0267	1·028	1·0343	1·0191	1·0012	1·0136
Sp. gr. of the Extract ...	1·0346	1·0366	1·0422	—	1·0118	1·0196
Extract	8·58	9·078	10·43	6·3	2·95	4·9
Alcohol	4·22	4·64	4·19	3·4	6·14	3·29
Sugar (as Glucose)......	1·53	1·47	2·24	1·02	0·42	0·67
Dextrin	—	5·4	—	—	—	—
Protein (Beer)	—	0·4	0·29	0·3	0·426	—
Protein (extract)	—	4·4	2·78	—	14·44	—
Viscosity..............	—	7′ 2″	10′ 1″	—	6′ 41″	7′ 4′
Strength..............	16·71	17·8	18·46	—	—	11·34
Ash..................	—	0·263	0·32	—	0·31	0·35
Acidity...............	—	8	—	—	12·4	—

E. N.

Effect of Coating Wheat with Oil. By I. PIERRE (*Ann. Chim. Phys.* [5], xii, 125—135).—The characteristics of good wheat are first described, and then it is pointed out that fraudulent endeavours are made to give semblance of those qualities to wheat which does not naturally possess them. One of the most common of these methods consists in coating the corn with a small quantity of oil, and particularly olive oil. The author describes experiments he has made with reference to the effect of this addition of oil to wheat in various known proportions; for his results, however, the original paper must be consulted. T. C.

Potassium Xanthate as an Antiseptic. By B. ZOLLER (*Deut. Chem. Ges. Ber.*, x, 52).—Urine, grape-juice, and other putrescible fluids, to which small quantities of this salt have been added, have been found to remain undecomposed for months.

The author confidently recommends the universal use of this salt for antiseptic purposes. C. F. C.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1876–77.

November 2nd, 1876.

Professor Abel, President, in the Chair.

Thomas H. Johnson, Fairfield, Liverpool; Otto Hehner, Holborn Viaduct, E.C.; George C. Thomson, Garnet Hill, Glasgow; Henry A. Bernays, Old Charlton, London; William J. Fuller, Bristol; and Gustav Auerbach, Sudbury, Harrow, were elected Fellows.

The following papers were read:—

"On the Oxides of Potassium:" by Sydney Lupton.

"On certain Bismuth Compounds:" by M. M. P. Muir.

"On Phospho- and Arseno-Cyanogen:" by W. R. Hodgkinson.

"A Secondary Oxidized Product formed during the reduction of Stannic Ethide:" by W. R. Hodgkinson and G. C. Matthews.

"A Preliminary Notice on *Pigmentum nigrum*, the Black Colouring Matter contained in Hair and Feathers:" by W. R. Hodgkinson and H. C. Sorby.

November 16th, 1876.

Professor Abel, President, in the Chair.

"Edward H. W. Swete, Rainbow Hill, Worcester; and Channell Law, Champion Park, Camberwell, were elected Fellows.

The following papers were read:—

"On Barwood:" by the late Professor Anderson.

"The Alkaloïds of the Aconites, Part I, on the Crystallisable Alkaloïds contained in *Aconitum Napellus*:" by Dr. C. R. A. Wright.

"On Potassium Triiodide:" by G. S. Johnson.
"On the Coal Gas of the Metropolis:" by T. S. D. Humpidge.

December 7th, 1876.

Dr. Gladstone, Vice-President, in the Chair.

Walter Charles Davis, Westury Park, Bristol; John Clark, Bath Street, Glasgow; Thomas Tyrer, Battersea, S.W.; F. H. Marshall, Middlesbrough-on-Tees; John Wood, Maryport, Cumberland; J. F. King, Edinburgh; and Charles Cecil Capel, Foot's Cray, Kent, were elected Fellows.

The following papers were read:—

"On Coleïn:" by A. H. Church.
"On Phenylenediamine:" by Otto N. Witt.
"On Calcium Sulphate:" by J. B. Hannay.
"Additional Notes on Potassium Triiodide:" by G. S. Johnson.

December 21st, 1876.

Professor Abel, President, in the Chair.

The following papers were read:—

"A further Study of Fluid Cavities:" by W. N. Hartley.
"On Thymoquinone:" by H. E. Armstrong.
"On High Melting Points, with special reference to those of Metallic Salts," Part II: by T. Carnelley.
"On the Estimation of Urea:" by G. Turner.
"On the Corrosion of Lead by the New River Company's Water:" by G. Bischof.

January 18th, 1877.

Professor Odling, Vice-President, in the Chair.

William Hampton, Hanley; D. W. Ladley, Cloudalkin, Dublin; and John Comyns Leach, Newton Blandford, were elected Fellows.

The following papers were read:—

"On some Derivatives of Dithymoltrichlorethane:" by Dr. Jäger.
"Preliminary Account of some Reactions in Organic Chemistry, and their Ultimate bearings:" by H. W. Hake and C. T. Kingzett.

"On Dinitroso-orcin and Dinitro-orcin:" by J. Stenhouse and C. E. Groves.

"On High Melting Points, with special reference to those of Metallic Salts, Part III:" by T. Carnelley.

February 1st, 1877.

Professor Abel, President, in the Chair.

A. G. Phillips, Liverpool, and F. Kopfer, Tübingen, Germany, were elected Fellows.

The following papers were read:—

"On Kekulé's and Ladenburg's Benzene Symbols:" by H. E. Armstrong.

"On the Formation of Coumarin, of Cinnamic Acid, and of other analogous Acids from the Aromatic Aldehydes:" by W. H. Perkin.

February 15th, 1877.

Dr. Gilbert, Vice-President, in the Chair.

Michael Conroy, New Brighton, Cheshire; Arthur Pearson Luff, St. Mary's Hospital, Paddington; John Angell, Manchester; Joshua Bardsley, Lancashire; Matthew A. Adams, Maidstone, Kent; and Peter Townsend Austen, New York, were elected Fellows.

The following papers were read:—

"On the Estimation of Urea by means of Hypobromite:" by A. Dupré.

"On a New Carbometer for the Estimation of Carbonic Anhydride:" by S. T. Pruen and G. Jones.

"On the Influence Exerted by Ammonium Sulphide in Preventing the Action of Various Solutions on Copper:" by F. W. Shaw and T. Carnelley.

"An Experimental Inquiry as to the Changes which occur in the Composition of Water from Wells near the Sea:" by W. Watson.

"On the Solvent Action of Various Saline Solutions on Lead:" by M. M. P. Muir.

"Derivatives of Di-isobutyl:" by W. Carleton Williams.

"Notes on Madder Colouring Matters:" by E. Schunck and H. Roemer.

March 1st, 1877.

Professor Abel, President, in the Chair.

Edward Hunter, Manchester; F. C. C. Hewett, Halifax, Nova Scotia; William Terrell, Swansea; Alexander Kinninmont, Glasgow; John Borland, Rosebank, Kilmarnock; W. Handsel Griffiths, Dublin; and George A. C. Pearce, Danes Inn, W.C., were elected Fellows.

Professor Thorpe delivered a Lecture on the Theory of the Bunsen Lamp.

March 15th, 1877.

Professor Abel, President, in the Chair.

F. W. Young, Warrington, was elected a Fellow.

The following papers were read:—

"Isomeric Nitrosoterpenes:" by W. A. Tilden and A. W. Shenstone.

"Preparation of Copper-zinc Couples:" by J. H. Gladstone and A. Tribe.

"On Chromium Pig Iron:" by E. Riley.

"Note on Gardenin:" by J. Stenhouse and C. E. Groves.

"Additional Note on a Process for Estimating Bismuth Volumetrically:" by M. M. P. Muir.

"On Certain Bismuth-compounds:" by M. M. P. Muir.

"On the Estimation of Urea by means of Hypobromite:" by Maxwell Simpson and C. O'Keefe.

March 30th. (Anniversary Meeting).

See vol. i, p. 493.

April 5th, 1877.

Professor Odling, Vice-President, in the Chair.

Professor N. S. Maskelyne delivered a Lecture "On the Discrimination of Crystals by their Optical Characters."

April 19th, 1877.

Dr. Gladstone, President, in the Chair.

The following papers were read :—

"On the Estimation of Manganese in Spiegeleisen, and of Manganese and Iron in Manganiferous Iron Ores:" by E. Riley.

"On a Method of Detecting Small Quantities of Bismuth:" by M. M. P. Muir.

"On Certain Bismuth-compounds," Part V: by M. M. P. Muir.

"Notes on Madder Colouring Matters, Munjistin, Purpurin, and Purpuroxanthic Acid:" by E. Schunck and H. Roemer.

May 3rd, 1877.

Dr. Gladstone, President, in the Chair.

The following papers were read :—

"On some points in Gas Analysis:" by J. W. Thomas.

"Experiments on the Decomposition of Nitric Oxide by Pyrogallate of Potash:" by Dr. Russell and W. Lapraik.

"Contributions to the History of the Naphthalene Series. No. 1. Nitros-β-Naphthol:" by J. Stenhouse and C. E. Groves.

"On Asbestos Cardboard and its uses in the Laboratory:" by W. N. Hartley.

May 17th, 1877.

W. Crookes, F.R.S., Vice-President, in the Chair.

The following papers were read :—

"On a Slight Modification of Hofmann's Vapour-density Apparatus:" by M. M. P. Muir and S. Suguira.

"Note on the Fluid contained in a Cavity in Fluor-spar:" by J. W. Mallet.

"Examination of Substances by the Time Method:" by J. B. Hannay.

"On the Dehydration of Hydrates by the Time Method. Part I. Iron and Aluminium Hydrates:" by W. Ramsay.

"On the Transformation of Aurin into Rosaniline:" by R. S. Dale and C. Schorlemmer.

May 31st, 1877.

Extraordinary General Meeting.

June 7th, 1877.

Dr. Gladstone, President, in the Chair.

The following papers were read:—

"On the Gases enclosed in Lignite-coal and Mineral-resin from Bovey Heathfield:" by J. W. Thomas.

"An Apparatus for Gas Analysis:" by E. Frankland.

"On Narcotine, Cotarnine, and Hydrocotarnine:" Part V, by C. R. A. Wright.

"On Otto of Limes:" by C. H. Piesse and C. R. A. Wright.

"On Primary Normal Heptyl Alcohol and some of its Derivatives:" by C. F. Cross.

"On the Transformation of Aurin into Rosaniline:" by R. S. Dale and C. Schorlemmer.

June 21st, 1877.

Dr. Gladstone, President, in the Chair.

F. H. T. Allen, Wakefield; H. S. Bell, South Kensington; C. T. V. Buck, Christ Church, Oxford; J. Y. Buchanan, Edinburgh; A. E. N. Franchimont, Leyden, Holland; J. Gardener, Camden-square, N.W.; W. Lapraik, Southgate-road, N.; G. A. Milne, Malton, Yorkshire; J. Napier, Ipswich; C. G. Neison, Royal Veterinary College, N.W.; J. L. Nolters, Netley; J. H. Poland, Blackheath, S.E.; J. Scarf, City of London School, E.C.; H. Senier, Finsbury Park, N.; H. G. Stacey, High Holborn, W.C.; S. G. Thomas, Wandsworth, S.W.; B. Thompson, Northampton; F. W. Jones, Camden-road, N.W.; A. Watt, Liverpool; W. Webster, jun., Lee, S.E.; and J. R. Young, Warrington, were elected Fellows.

The following papers were read:—

"On the Action at a High Temperature of certain Volatile Metallic Chlorides on certain Hydrocarbons:" by Watson Smith.

"On the Action of Alkaline Oxalates on the Earthy Carbonates, and of Solutions of Alkaline Carbonates on the Earthy Oxalates:" by Watson Smith.

"On Thallious Platinocyanide:" by R. J. Friswell and A. J. Greenaway.

"On Crystallised Barium Silicate:" by E. W. Prévost.

"Note on Anethol and its Homologues:" by W. H. Perkin.

"Note on Persulphocyanic Acid:" by R. W. Atkinson.

"On the Oxidation-products of Aloïns:" by W. Tilden.

Donations to the Library, 1876–77:—

"Chemical and Physical Researches:" by Thos. Graham, D.C.L., F.R.S.; edited by James Young, F.R.S., and R. Angus Smith: from the Editors.

"Experimental Researches in Pure, Applied, and Physical Chemistry:" by E. Frankland, F.R.S.: from the Author.

"Inorganic Chemistry." 2 vols.: by T. E. Thorpe, Ph.D., F.R.S.: from the Author.

"Chemistry, General, Medical, and Pharmaceutical:" by John Attfield. 7th Edition: from the Publisher.

"The Primer of Chemistry, including Analysis:" by A. Vacher: from the Author.

"Chemical Handicraft:" by J. J. Griffin: from Messrs. Griffin.

"The History, Products, and Processes of the Alkali Trade:" by Chas. T. Kingzett: from the Author.

"Instruction in Photography:" by Capt. Abney, F.R.S.: from the Author.

"Composition of Foods, Waters, Minerals, Manures, and Miscellaneous Substances:" compiled by E. T. Kensington, F.C.S.: from the Author.

"Food-tables:" by J. B. Lyon, Surgeon-Major: from the Author.

"A Treatise on the Law relating to the Pollution and Obstruction of Watercourses:" by Clement Higgins, M.A., F.C.S.: from the Author.

"Anthracene; its Constitution, Properties, Manufacture, and Derivatives:" by G. Auerbach: translated and edited by Wm. Crookes, F.R.S.: from the Editor.

"Report to the Secretary of State for the Home Department on the Subject of Testing Petroleum:" by F. A. Abel: from the Author.

"Report of the Royal Commissioners appointed to Inquire into the Spontaneous Combustion of Coal in Ships:" from F. A. Abel, Esq.

"Contributions from the Chemical Laboratory of Harvard College:" by J. P. Cooke: from the Author.

"New South Wales, its Resources and Progress:" by authority of the Commissioners of the Philadelphia Exhibition of 1876:" from Prof. Liversidge.

"Mines and Mineral Statistics of New South Wales:" compiled by the Hon. John Lucas, M.P.: from Prof. Liversidge.

"Mineral Map and General Statistics of New South Wales:" from Prof. Liversidge.

"Smithsonian Contributions to Knowledge." Vols. xx and xxi: from the Smithsonian Institution.

"Ausführliches Lehrburch der Chemie:" von H. E. Roscoe und C. Schorlemmer. Band I: from the Authors.

"Chemische Mittheilungen aus dem Laboratorium der technischen Chemie in Prag.:" von Dr. Franz. Stolba: from the Author.

"Recherches sur les substances explosives; combustion de la Poudre:" par MM. Noble et Abel; traduit de l'Anglais par MM. le Lieut.-Col. Aloncle et le Commandant Heden: from F. A. Abel, Esq.

"Études sur les Echinoïdes:" par S. Loüen (Atlas): from the Royal Swedish Academy of Science.

Pamphlets:—

"Nature of the Physical Forces: by Edward Vogel:" from the Author.

"Transverse Absorption of Light:" by William Akroyd:" from the Author.

"Experiments on the Maximum Elasticity and Density of Vapours:" by A. Morton: from the Author.

"Examples of Pseudocrystallisation:" by Prof. Liversidge: from the Author.

"A New Form of Polariscope, and its Application to the Observation of the Sky:" by H. H. M. Bosanquet: from the Author.

"On the Effect of Heat on the Chloride, Bromide, and Iodide of Silver:" by G. F. Rodwell:" from the Author.

"Note on the Resistance of Materials, as affected by Flow and Rapidity of Distortion:" by R. H. Thurston: from the American Society of Civil Engineers.

"The Rate of Set of Metals subjected to Strain for considerable Periods of Time:" by R. H. Thurston: from the Author.

"On the Formation of Moss Gold and Silver:" by A. Liversidge: from the Author.

"Scheele's Green: its Composition as usually prepared, and some Experiments upon Arsenite of Copper:" by P. S. Sharples: from the Author.

"Schweinfurt Green:" by P. S. Sharples: from the Author.

"On Franklandite, a New Mineral Borate:" by J. Emerson Reynolds: from the Author.

"On the Composition of Lievrite, as determined by Mr. Early's Method:" by J. Emerson Reynolds: from the Author.

"On a Remarkable Example of a Contorted Slate:" by A. Liversidge: from the Author.

"Fossiliferous Siliceous Deposit from the Richmond River, N.S.W.:" by A. Liversidge: from the Author.

"On the So-called 'Greenstones of Western Cornwall:'" by J. A. Phillips: from the Author.

"Remarks on the Sedimentary Formations of New South Wales:" by the Rev. W. B. Clarke: from Prof. Liversidge.

"Notes on the Iron and Coal Deposits, Walleraway, and on the Diamond Fields:" by Prof. Liversidge: from the Author.

"On Rain-fall, Evaporation and Percolation:" by Dr. Gilbert: from the Author.

"On the Rainfall for 25 years (1851—1875) as observed at the Radcliffe Observatory, Oxford:" by the Rev. R. Main: from the Author.

"The Composition of the Water supplied to London during 1876:" by C. M. Tidy: from the Author.

"The Main Drainage of Oxford:" by W. H. White: from the Author.

"On the Mineral Water discovered in Sinking the Artesian Well at St. Clement's, Oxford:" by Joseph Prestwich, M.A., F.R.S.: from the Author.

"Influence of Chemical Constitution and Physiological Activity:" by J. Emerson Reynolds, M.D.: from the Author.

"On some Points in connection with Animal Nutrition:" by J. H. Gilbert: from the Author.

"The Formation of Fat in the Animal Body:" by J. B. Lewis and J. H. Gilbert: from the Authors.

"On the Analysis of Milk: its Composition, and the Quality of the Milk sold in Dublin and its Suburbs:" by E. H. Cook: from the Author.

"On Noctilucin:" by Dr. T. L. Phipson: from the Author.

"Note on the Administration of Phosphorus:" by Edward Squibb, M.D.: from the Author.

"The Use and Value of Arsenic in the treatment of Diseases of the Skin:" from the Author.

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"Report on the Sugar Cane Disease in the Mary River District, Queensland:" by Prof. Liversidge: from the Author.

"On the Estimation of Nitrous and Nitric Acids:" by G. Lunge: from the Author.

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"A Plan for rendering Salted Meat more Nutritious, thereby preventing Scurvy:" by Robt. Galloway: from the Author.

"Truth *in Extremis:*" a Plea against the Murder of Science by the Gold-Poison:" by a Searcher: from the Author.

"American Contributions to Chemistry: an Address delivered on the occasion of the celebration of the Centennial of Chemistry at Northumberland, Pa., Aug. 1, 1874:" by Benjamin Silliman, of Yale College: from the Author.

"Ueber verschiedene Amylene und Amylalkohole:" von A. Wischnegradsky: from the Author.

"Die Naturgesetze, und ihr Zussammenhang mit den Abstracten Wissenschaften:" von Hermann Scheffler, 2 Theile: from the Author.

"La Loi de Dulong et Petit:" par A. Terreil: from the Author.

"Sur les Equivalents Chimiques et les Poids Atomiques, comme Bases d'un Système de Notation:" par C. Marignac: from the Author.

"Expériences Pratiques de la Boussole Circulaire, faites à bord des navires de l'Etat et de la Marine Mercantile:" par E. M. Duchemin: from the Author.

"Sur une méthode générale de Synthèse d'Hydrocarbures, d'Acetones," &c.: par C. Friedel et J. Crafts: from the Authors.

"Sur l'Isodibutylene, l'une des variétés Isomériques de l'Octylène:" par M. Boutlerow: from the Authors.

"Recherches sur les Acides Tetra- et Trithioniques:" par M. M. W. Springet et A. Lèvy: from the Authors.

"Saggi di Esperienze Agrarie:" fatte dal Prof. E. Becchi.—Fascicoli, 1—5: from the Author.

"Nuove Ricerche Chimiche su l'Acqua Salso-iodica di Castrocaro:" fatte dal Prof. E. Becchi: from the Author.

"Ricerche Chimiche su l'Acqua Ferro-Manganesifera delle Piazzule di Proprietà della Contessa Luisa Cappini:" fatte dal Prof. E. Bècchi: from the Author.

Periodicals:—

"Philosophical Transactions for 1876:" from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1876:" from the Royal Society.

"Memoirs of the Royal Astronomical Society," Vol. xliii, 1875–1877: from the Society.

"Transactions of the Royal Society of Edinburgh." Vol. xxvii. Part IV (1875–76).

"Proceedings of the same. Session 1875–1876:" from the Society.

"Transactions of the Royal Irish Academy." Vol. xxvi, 1876: from the Academy.

"Monthly Notices of the Royal Astronomical Society, 1876-77:" from the Society.

"Proceedings of the Royal Institution of Great Britain," Vol. ix: from the Institution.

"Reports of Friday Evening Lectures at the Royal Institution, 1876:" from the Institution.

"Quarterly Journal of Science," Vol. vii: from the Editor.

"Quarterly Journal of the Geological Society, 1876—77:" from the Society.

"Journal of the Iron and Steel Institute, 1877:" from the Institute.

"Year-book of Pharmacy, 1876 and 1877:" from Professor Attfield.

"Pharmaceutical Journal and Transactions." Third series, Vol vi: from the Pharmaceutical Society.

"The Photographic Journal, Vols. i, ii:" from the Photographic Society.

"Journal of the Society of Arts, 1876-77:" from the Society.

"The Textile Colourist." Edited by Charles O'Neile, F.C.S., 1877: from the Editor.

"Report of the British Association for the Advancement of Science, 1875 (Bristol):" from the Association.

"The Mineralogical Magazine, 1877:" from the Mineralogical Society.

"Nature, 1876-77:" from the Editor.

"The Chemical News, 1876-77:" from the Editor.

"The Telegraphic Journal and Electrical Review, 1876-77:" from the Editor.

"Engineering, 1876-1877:" from the Editor.

"The Druggist, 1877:" from the Editor.

"The Chemist and Druggist, 1877:" from the Editor.

"Forty-third and Forty-fourth Reports of the Royal Cornwall Polytechnic Society, 1875 and 1876:" from the Society.

"Transactions of the Newcastle-on-Tyne Chemical Society:" Vol. iii. 1874-1877: from the Society.

"Memoirs (Vol. v) and Proceedings (Vol. xv) of the Literary and Philosophical Society of Manchester:" from the Society.

"Annual Report of the Yorkshire Philosophical Society for 1875:" from the Society.

"Third Annual Report of the Yorkshire College of Science, Leeds:" from the College.

"Journal of the Literary and Philosophical Society of Liverpool, 1875-1876:" from the Society.

"Transactions (Vol. xii) and Proceedings (Vol. lii) of the Cambridge Philosophical Society:" from the Society.

"Western Review of Science and Industry, 1877:" from the Editor.

"Transactions of the Philosophical Society of New South Wales, 1862–1868:" from the Society.

Transactions and Proceedings of the Royal Society of New South Wales." Vol. ix, 1876: from the Society.

"American Journal of Science and Arts." Vols. xii, xiii: from the Editors.

"Journal of the Franklin Institute, 1877:" from the Institute.

"Transactions of the American Philosophical Society." Vol. xv. Part II. (1875): from the Society.

"Proceedings of the American Philosophical Society, January to June, 1877:" from the Society.

"Smithsonian Report for 1876:" from the Smithsonian Institution.

"Report of the Commissioner of Agriculture (U.S.) for 1875:" from the Commissioner.

"American Chemist, 1877:" from the Editor.

"Bulletin of the Bussy Institution, Boston," Part v, 1876: from the Institution.

"Proceedings of the Academy of Natural Sciences at Philadelphia, 1876:" from the Academy.

"Transactions of the American Medical Association, 1876:" from the Association.

"Proceedings of the American Academy of Arts and Sciences, 1877:" from the Academy.

"Memoirés et Comptes rendus de la Société des Sciences Medicales de Lyons." Tome xiv, 1874: from the Society.

"Moniteur Scientifique, 1876–77:" from the Editor.

"Revue Scientifique, 1877:" from the Editor.

"Les Mondes, 1875–76:" from the Editor.

"Mémoires de l'Académie des Sciences et Lettres de Montpellier." Section des Sciences. Tomes 1875: from the Academy.

"Bulletin de l'Académie Royale des Sciences de Belgique, 1875–1876:" from the Academy.

"Annuaire de l'Académie Royale des Sciences de Belgique, 1875–1876:" from the Academy.

"Bulletin de l'Académie Imperiales des Sciences de St. Pétersbourg." Tome xxiv: from the Academy.

"Bulletin de la Société Industrielle et Agricole d'Angers et du Département de Maine et Loire, 1875." 1er Trimestre: from the Society.

"Société Hollandaise des Sciences de Harlem: Notices historiques, &c." Janvier, 1876: from the Society.

"Archives Néerlandaises des Sciences Exactes et Naturelles." Tome xi: from the Editor.

"Atti della Real Accademia dei Lincei." Anno cclxxiv (1876–77): from the Academy.

"Memorie dell' Accademia delle Scienze dell' Istituto di Bologna." Serie 3. Tomi v, vi: from the Academy.

"Rendiconti delle Sessioni della stessa Accademia, 1874–75:" from the Academy.

"Monatsbericht der Königlich-preussischen Akademie der Wissenschaften zu Berlin." 14 Bände, 1862–1875, 1866–1877: from the Academy.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften." 34-ter Band: from the Academy.

"Sitzungsberichte derselben," 1874. Zweite Abtheilung, Nos. 8—10. 1875; Zweite Abtheilung, Nos. 1—5.

"Abhandlungen der Königlich-Bayerischen Akademie der Wissenschaften." 12-ter Band. Zweite Abtheilung. 1876: from the Academy.

"Sitzungsberichte derselben, 1876:" from the Academy.

"Jenaische Zeitschrift fürNaturwissenschaft." 12-ter Band. Supplement: from the Editor.

"Muster-Zeitung, Zeitschrift für Färberei, Drückerei, Bleicherei, u. s. w." No. 39 (1875): from the Editor.

"Verhandlungen der Naturforschenden Gesellschaft in Basel." 6-ter Theil. 2-ter Heft (1875): from the Society.

"Verhandlungen der Physikal-Medicinischen Gesellschaft zu Würzburg." 11-ter Band. 1 und 2 Heft: from the Society.

"Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich." 19-ter und 20-ter Jahrgang: from the Academy.

"Archiv für die Naturkunde Liv-, Esth-, und Kur-lands." Band i. Heft 8: from the Philosophical Society of Dorpat.

"Chemische Mittheilungen aus dem Laboratorium der Technischen Chemie in Prag:" von Dr. Franz Stolba: from the Author.

"Mandblaad voer Naturwetenschappen, January to May, 1877:" from the Philosophical Society of Amsterdam.

"Oversigt over det Kongelige Danske Viderskabernes Selskabs Forhandlinger, og des Medlemmers Arbeeten:" from the Royal Danish Academy of Sciences.

Kongl. Vetenskaps Akademiens Handlingar, 1874, 1875:" from the Royal Swedish Academy of Sciences.

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